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THE SPONTANEOUS COMBUSTION OF COAL

WITH SPECIAL REFERENCE TO BITUMINOUS COALS
OF THE ILLINOIS TYPE

BY

S. W. PARR

AND

F. W. KRESSMANN



UNIVERSITY OF ILLINOIS
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UNIVERSITY OF ILLINOIS

ENGINEERING EXPERIMENT STATION

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DECEMBER 1910

THE SPONTANEOUS COMBUSTION OF COAL

WITH SPECIAL REFERENCE TO BITUMINOUS COALS OF THE ILLINOIS TYPE

BY S. W. PARR, PROFESSOR OF APPLIED CHEMISTRY AND
F. W. KRESSMANN, GRADUATE ASSISTANT IN
APPLIED CHEMISTRY

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TO THE
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THE SPONTANEOUS COMBUSTION OF COAL
WITH SPECIAL REFERENCE TO BITUMINOUS
COALS OF THE ILLINOIS TYPE

I. INTRODUCTION

The coal production in Illinois, in 1907 and also in 1908, amounted, each year, to 51 million tons, valued at 52 million dollars. There was a slight increase in 1908 over the tremendous production in 1907, in spite of the labor troubles which caused a complete shut-down of mining, beginning with the April, 1908, conference of miners and operators. The general business depression of that year caused many consumers to use the cheaper grades of bituminous coals in preference to the more expensive anthracite, and, since production at the mines was thus stimulated before and after the shut-down, the public felt no shortage of fuel. Such a situation is unnecessarily expensive both for the consumer and the miner, as a uniform daily output is necessary in order to procure and maintain the most economical production of coal. However, having secured such a uniform daily output, it is manifest that a production of coal so great as that given above cannot be guaranteed to meet fluctuations in daily demand.

To guard against unknown and unforeseen conditions, such as labor difficulties, variations in output or delay in transportation, the large manufacturing interests are beginning to see the need of storing large amounts of reserve fuel. Variations, due to seasonable demands of fuel for domestic purposes, also necessitate the storage of coal either by the mining interests or by the coal dealers. In the maritime world, the storage of coal is one of the great problems of today. Our large battle ships and ocean greyhounds use upwards of 500 tons of coal per day, and hence coal must not only be stored on shipboard, but large reserve supplies must be on hand at the various coaling stations.

On the other hand, wherever large quantities of bituminous coal are stored,—and bituminous coal furnishes by far the greatest part of the energy used at the present day,—the danger aris-

ing from spontaneous combustion must be taken into consideration, and hence elaborate and costly measures are being taken to avert this hidden peril. The problem of spontaneous combustion is rapidly being recognized as the great problem in the storage of bituminous coals.

The United States government, which uses upwards of a quarter of a million tons of coal yearly for the navy alone, has taken great precautions to avert the danger of spontaneous combustion in its new coal pile at Bradford, on Narragansett Bay, near Newport, where the storage capacity is about 60 000 tons.

The coal bins or pockets are provided with temperature tubes, so that if incipient heating should occur it will be discovered and located long before a temperature has been reached at which combustion commences. These tubes consist of lengths of 4 in. galvanized pipe about 20 feet long, set in the bin floors and projecting upwards through the coal pile. They contain thermostats which are arranged to indicate temperatures in excess of 150°F . Circuits are run from the 232 tubes to a general annunciator in the superintendent's office, so that if heating does occur an alarm is at once sounded and the exact position of the pile where the heating has developed is shown on the indicator.

The temperature of 150°F . was decided upon as the danger point as the result of numerous experiments made by the Navy Department which indicated that if the temperature of the coal reached this point the increase in temperature beyond was very rapid.¹ At the New York Navy Yard, compartments of 525 gross tons capacity have been built. The floors of these bins are of portland cement, and the side walls are made of a mixture of portland cement, sand, and anthracite boiler cinders. The roofs are of iron².

The danger of spontaneous combustion on shipboard is even greater than during ordinary storage, for the coal is usually stored in whatever space is unoccupied by other materials, usually at the side of the vessel between the boiler rooms and the side planking. Here the coal is subjected to the heat of the boiler and engine rooms, and is especially liable to ignite spontaneously.

Up to the present time a great deal of excellent work together with a considerable amount of theorizing regarding the nature and cause of spontaneous combustion has been done, but the

¹Chemical Engineering, June 1906

²Engineering News, July 21, 1904, page 68

views presented have been very contradictory, as a study of the Appendix will reveal. It seemed probable, therefore, that the differences in the particular varieties of coal worked with might have been the cause of the various theories advanced, and that seeming truths and generalizations drawn from work on a specific coal are not applicable to coals in general.

On assembling the results of many investigations in this field, it was found that the primary conditions which lead to spontaneous combustion are considered to be as follows:

- (1) The presence of pyrite.
- (2) The size of coal.
- (3) The initial or induced temperature of the coal.
- (4) The presence of moisture.

While these results are extremely suggestive, they cannot be looked upon as conclusive or necessarily applicable to the problems in this region connected with coal storage. Two reasons, at least, may be given in support of this statement. (1) Such an assembling of results gives no suggestion as to the relative importance of the various influences. (2) The conclusions of an investigator based upon experiments with one type of coal might not apply in the case of a coal differing in texture and chemical composition. These two features must be understood for any given type of coal before any safe statements can be made regarding that particular region. For example, while it may be true of any coal that the above enumerated causes are operative, it is more important in any case to know the order of their importance. Again, in the case of coals from the midcontinental fields, i. e., of the Illinois type, a peculiarity of the composition exists which may enter into the problem as a factor. The coals of this region, for example, are characterized by a high content of moisture seldom below 10 per cent and averaging 12 to 15 per cent at the vein. This is in marked contrast to coals of the same general type of the eastern United States and Europe, where this factor rarely exceeds 2 to 4 per cent. Again, this fact, while perhaps not so significant in itself is always accompanied by another item which may have some bearing in that this large water content is always accompanied by a higher content of oxygen combined as a part of the organic matter, in contrast with the lower oxygen content of the low moisture bituminous coals. Also, the high sulphur content of Illinois coal, ranging from 1 to 6 per cent, with

the average at about 4 per cent, may materially influence the spontaneous combustion of this type of coal.

The Illinois bituminous coals, with their high moisture and ash, varying amounts of sulphur and inert volatile matter, seem, therefore, to require special study in order to establish the reasons for their property of spontaneous combustion. The subject naturally divides itself into three subdivisions: first, the determination, if possible, of the causes of spontaneous combustion; second, the relative importance of these causes; and third, the removal, if possible, of this property of spontaneous combustion either through the treatment of the coal by chemical processes or through certain methods of handling.

II. OUTLINE OF EXPERIMENTAL INVESTIGATIONS

GENERAL DESCRIPTION OF METHODS AND APPARATUS

Coal from Williamson county, Illinois, marketed under the trade name of "New Ohio," was used for these experiments. The composition of the various samples will be found on pages 9 and 14. About one-half ton of large lumps was required for the experiments. These lumps were ground to the requisite sizes. The grinding was done in a small Chipmunk crusher and the ground coal was then run through a revolving screen, by which it was sized. The screen used was of the revolving or trommel type, made of perforated steel plate about 6 ft. long and 1 ft. in diameter, in which holes of the following sizes were drilled: $\frac{1}{8}$ inch, $\frac{1}{4}$ inch, $\frac{3}{8}$ inch, $\frac{1}{2}$ inch, $\frac{3}{4}$ inch, 1 inch. The coal coming through the $\frac{1}{4}$ inch holes, known as size $\frac{1}{8}$ - $\frac{1}{4}$ was always screened twice because a small amount of dust escaped the $\frac{1}{8}$ -inch holes the first time; in order to make the $\frac{1}{8}$ - $\frac{1}{4}$ size dust-free it was re-screened. Each time only enough coal was ground and screened to meet immediate demands and any left over was thrown away, so that the coal used was always fresh and unoxidized.

The most potent elements in the case were believed to be temperature, fineness of division, pyrites and the amount of moisture present. These are taken up in the order given.

1. *Effect of Temperature and Size.*—In studying the effect of external temperature the general principle was adopted of placing rather large, 25 to 35 lb., samples within an insulated space,

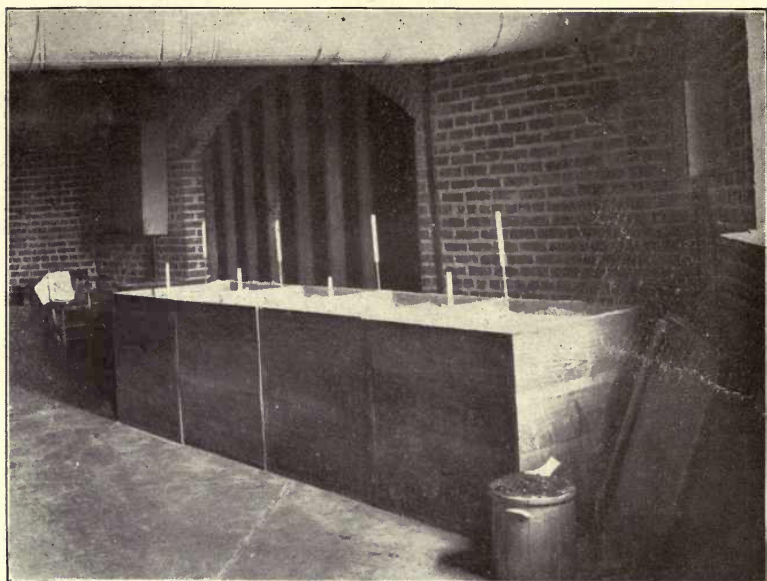


FIG. 1.
GENERAL VIEW OF THE OVENS, SHOWING THERMOMETER ARRANGEMENT
AND A SAMPLE JAR OF COAL.

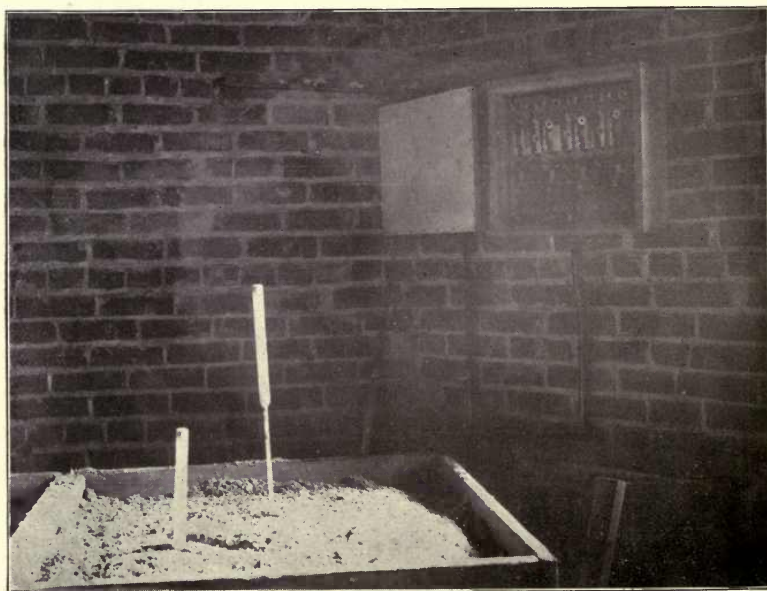


FIG. 2.
A VIEW OF THE TEMPERATURE REGULATING APPARATUS AND
DETAIL OF ONE OF THE OVENS.

where the atmosphere immediately surrounding the sample could be kept under exact control. By means, then, of thermometric readings taken within the coal mass and also from the atmosphere of the chamber, any oxidation within the coal sample would be indicated by a rise of temperature above that of the surrounding atmosphere. The details as to the time, temperature, construction and general procedure were as follows:

2. *Methods and Apparatus.*—The coals were placed in the constant temperature ovens for a period of three days each, as, in the preliminary experiments that were run, it was found that a period of 72 hours was sufficient to give the maximum rise in temperature. The following temperatures were maintained in four different ovens; 40°, 60°, 80°, 115° Centigrade. The coal was first placed in the 40° oven, and after a period of three days, it was moved to the 60° oven; after another period of three days, it was moved to the 80° oven; and finally, after another period of three days, it was moved to the 115° oven; after remaining in this oven for three days the coal was removed. A 5-gal. stone jar having the bottom perforated with $\frac{1}{2}$ -in. holes was used as a container for the coal. A jar of this size held a sample of coal weighing about 35 or 40 lb.

The ovens were constructed as follows. They consisted of two wooden boxes, one set inside the other. The boxes were in the form of cubes, the outer box being a 3-ft. cube made of 1½-in. pine boards; the inner box was also in the form of a cube, made of the same material only it was 8 in. smaller than the outside box. This left a space of 4-in. on all sides between the two boxes, and this space was tightly packed with mineral wool, the inner box being well insulated in this manner. Across one corner of the inner box a board was nailed. This board was 4 in. shorter than the box and was nailed into the box so as to leave a clear space of 2 in. at the top and bottom of the box. The triangular space formed by this board and the corner of the box was lined with $\frac{1}{4}$ -in. asbestos board so as to insulate it. This space then formed a chimney, and near the bottom of this chimney the electric lights used to heat the boxes were hung. The temperature was regulated by means of a mercury regulator which consisted of a large bulb of mercury expanding up a capillary tube. A platinum wire was fused into the bulb so as to be in contact with the mercury. Down the top of the capillary tube a long, fine

needle was placed so that when the mercury was expanded to a certain height at a definite temperature the mercury would just come in contact with the needle. Wires were run from the regulator to a telegraph relay, the mercury regulator being connected in series in this circuit. This outfit was run by storage battery current. The telegraph relay was used to make and break the 220-volt circuit on which the lights used for heating were connected.

The jars of coal were placed on several bricks in the inner box, the bricks being arranged so as to elevate the jar high enough so that it would be in the middle of the box, and also to allow the air around the jar to circulate freely. The cover of the inner box was then put into place, and through the holes in the latter several long thermometers (about $2\frac{1}{2}$ ft. long) were placed to indicate the temperature of the air in the box and also the temperature of the coal. The thermometers used to indicate the temperature of the air in the box were placed so that one was near the heating chimney and the other was at a point farthest from it. The thermometer used to indicate the temperature of the coal was placed so that the bulb was 4 or 5 in. below the surface of the coal. Readings of these temperatures in degrees Centigrade were taken every morning and afternoon.

In the first run, called Series 1, five sizes of the coal were used. These samples were not what would be known as air-dry, because the coal was used as soon as it was ground; the large lumps, however, were air-dry. The five sizes were as follows:

Size 0: This size included some of the coal that went through the smallest holes in the screen and then was ground in a disk pulverizer until it was very finely divided. About 75 per cent of this size went through a 120-mesh screen, and all of it went through an 80-mesh.

Size 0- $\frac{1}{8}$: This coal went through the $\frac{1}{8}$ in. holes in the large revolving screen.

Size $\frac{1}{8}$ - $\frac{1}{4}$: This coal went through the $\frac{1}{4}$ in. holes in the screen.

Size $\frac{1}{4}$ - $\frac{3}{8}$: This coal went through the $\frac{3}{8}$ in. holes in the screen.

Size $\frac{3}{8}$ - $\frac{1}{2}$: This size was a mixture of equal parts of the coal that went through the $\frac{1}{2}$ in. and the $\frac{3}{4}$ in. holes in the revolving screen; it was thought that there would not be enough difference between the results of the $\frac{1}{2}$ in. and the $\frac{3}{4}$ in. size, so the two were mixed in equal proportions.

DETAILS OF EXPERIMENTS

Experiments were conducted in 15 series. Each series represented experiments upon certain chosen sizes of coal, and all the coals of a given series were subjected to the same conditions. Each series differed from the others by one variable as to condition, such as dry or wet, varying content of pyrites, etc.

Composition of Coal. The composition of the coal used in the first five series, as indicated by a proximate analysis, was as follows:

TABLE 1

	Size 0- $\frac{1}{8}$ per cent	Size $\frac{1}{8}$ - $\frac{1}{4}$ per cent
Moisture.....	4.16	4.62
Volatile Matter.....	33.48	33.37
Fixed Carbon.....	50.86	50.88
Ash.....	11.50	11.13
Total.....	100.00	100.00
Sulphur.....	1.26	1.29

Calculated to Dry Coal

Volatile Matter.....	34.92	34.78
Fixed Carbon.....	53.08	53.58
Ash.....	12.00	11.64
Total.....	100.00	100.00
Sulphur.....	1.32	1.35

The pyritic iron was determined by taking the difference between the total iron in the coal and the iron soluble in dilute hydrochloric acid. The results for the above two samples are as follows:

	Size 0- $\frac{1}{8}$ per cent	Size $\frac{1}{8}$ - $\frac{1}{4}$ per cent
Total iron.....	1.91	1.73
HCl soluble Fe.....	0.73	0.67
Pyritic iron.....	1.18	1.06
Calculated.....		
Pyrite content.....	1.76	1.60

Inasmuch as more of the larger sizes were used than the finer,

the average pyrite content of the coal was taken as 1.65 per cent.

Series 1.—A jar of each of the four largest sizes of coal was placed in the ovens in the same increasing ratio of size of the coal and the temperature of the oven, e. g., size 0- $\frac{1}{8}$ was put in the 40° oven, size $\frac{1}{8}$ - $\frac{1}{4}$ in the 60° oven, size $\frac{1}{4}$ - $\frac{3}{8}$ in the 80° oven, and size $\frac{3}{8}$ - $\frac{1}{2}$ in the 115° oven. This method of procedure was adopted to save time, for by this means all the ovens could be filled at once, and since it took 12 days for a coal to pass through the four ovens, a considerable saving of time resulted, and the large sizes of coal were not oxidized to an appreciable extent at these low temperatures. After the coals had remained in the ovens for three days, they were moved up to the next oven, size $\frac{3}{8}$ - $\frac{1}{2}$ was taken out of the 115° oven and the next smaller size put in, and size 0 was put in the 40° oven. The reading of the temperatures was made in the morning and afternoon, chiefly to see that the regulators were working well and that the lights were not burned out, and also to get the increase in temperature of the coal over that of the ovens. As is shown in Table 2, the

TABLE 2
SERIES 1—DRY COAL—1.65 PER CENT PYRITE

	Coal 0	Coal 0- $\frac{1}{8}$	Coal $\frac{1}{8}$ - $\frac{1}{4}$	Coal $\frac{1}{4}$ - $\frac{3}{8}$	Coal $\frac{3}{8}$ - $\frac{1}{2}$
Time in hours	96.0	89.0			
Oven temperature °C	38.8	40.0			
Coal temperature °C	41.7	42.5			
Rise temperature °C	2.9	2.5			
Time in hours	89.0	76.0	89.0		
Oven temperature °C	60.0	60.5	60.0		
Coal temperature °C	65.0	63.7	63.5		
Rise temperature °C	5.0	3.2	3.5		
Time in hours	77.0	74.0	76.0	89.0	
Oven temperature °C	80.0	80.0	79.8	77.0	
Coal temperature °C	95.0	91.1	89.7	78.0	
Rise temperature °C	15.0	11.1	9.9	1.0	
Time in hours	42.0				
Oven temperature °C	108.0				
Coal temperature °C	168.0				
Rise temperature °C	60.0				
Time in hours	72.0	89.0	74.0	76.0	89.0
Oven temperature °C	108.0	109.0	107.8	108.0	107.0
Coal temperature °C	154.0	140.0	133.2	127.9	122.4
Rise temperature °C	46.0	31.0	25.4	19.9	15.4

maximum rise in temperature in some cases took place before the end of three days. This was especially the case in the dry, finer sizes. The average temperature of the ovens and the temperature of the coal at the end of the three days are shown in Table 2.

Series 2. Series 2 was the same as Series 1, the only difference being that the coal in Series 2 was thoroughly wet before being placed in the ovens.

Before beginning Series 2, in order to get some idea as to the oxidation of the coal and the amount of oxygen used up by it, the air in the different ovens was analyzed, after the coal had been in the ovens for three days. The results were as follows:

	Oven 1—40°	Oven 2—60°	Oven 3—80°	Oven 4—115°
Per cent CO ₂	0.40	1.20	1.00	1.81
Per cent Oxygen.....	20.00	18.40	19.40	16.00

Since the oxygen content decreased so much, it was thought

TABLE 3

SERIES 2—WET COAL—1.65 PER CENT PYRITE

	Coal 0	Coal 0— $\frac{1}{8}$	Coal $\frac{1}{8}$ — $\frac{1}{4}$	Coal $\frac{1}{4}$ — $\frac{3}{8}$	Coal $\frac{3}{8}$ — $\frac{1}{2}$
Time in hours.....	72.0	81.0			
Oven temperature °C	38.5	38.5			
Coal temperature °C	38.3	38.5			
Rise temperature °C			
Time in hours.....	84.0	72.0	81.0		
Oven temperature °C	60.0	59.0	59.5		
Coal temperature °C	57.5	58.5	62.4		
Rise temperature °C	2.9		
Time in hours.....	72.0	84.0	72.0	81.0	
Oven temperature °C	80.0	80.0	80.0	80.0	
Coal temperature °C	86.5	85.5	86.3	85.6	
Rise temperature °C	6.5	5.5	6.3	5.6	
Time in hours.....	48.0				
Oven temperature °C	111.5				
Coal temperature °C	168.3				
Rise temperature °C	56.8				
Time in hours.....	72.0	72.0	84.0	72.0	81.0
Oven temperature °C	114.0	111.9	110.2	112.5	111.5
Coal temperature °C	164.8	148.2	131.0	128.0	125.5
Rise temperature °C	50.8	36.3	20.8	16.5	14.0

necessary to ventilate the ovens so as to maintain atmospheric conditions. This was done by boring several $\frac{1}{2}$ -in. holes through the walls of both boxes near the bottom and putting a $\frac{1}{2}$ -in. glass tube through the two walls. One of the tubes was placed so that the fresh cool air that came in was delivered at the bottom of the heating chimney, and the other tube delivered its air at the opposite side of the box. At the top of the box a take-off pipe of the same size was inserted.

Series 3.—In Series 3 and 4 the content of iron pyrites was increased over the amount in Series 1 and 2 so that the total of iron pyrites in the form of FeS_2 was 3 per cent. This was accomplished by taking some large lumps of pyrite just as it occurs in the coal measures of Vermilion County. This was ground to pass through a 20-mesh sieve, and upon analysis was found to be 87.62 per cent pure. This calculation of purity was based upon the sulphur content of the material, which was 46.73 per cent. In Series 3 the variable from Series 1 is in the content of pyrite which has been increased from 1.65 per cent to 3 per cent. Tests upon the two larger sizes were omitted for the reason indicated in Tables 2 and 3. The oxidation on these larger sizes was too small and not different in character from the reaction upon the finer sizes, hence they were omitted from the subsequent experiments.

TABLE 4
SERIES 3—DRY COAL—3 PER CENT PYRITE

	Coal 0	Coal 0- $\frac{1}{8}$	Coal $\frac{1}{8}$ - $\frac{1}{4}$
Time in hours.....	71.0	71.0	
Oven temperature °C.....	37.0	39.5	
Coal temperature °C.....	42.0	42.0	
Rise temperature °C.....	5.0	2.5	
Time in hours.....	72.0	71.0	71.0
Oven temperature °C.....	60.0	60.0	66.0
Coal temperature °C.....	68.2	67.5*	60.0
Rise temperature °C.....	8.2	7.5	6.0
Time in hours.....	72.0*	72.0	71.0
Oven temperature °C.....	75.0	80.0	81.5
Coal temperature °C.....	88.6	93.5	93.8
Rise temperature °C.....	13.6	13.5	12.3
Time in hours.....	30.0		
Oven temperature °C.....	115.0		
Coal temperature °C.....	190.3		
Rise temperature °C.....	75.3		
Time in hours.....	72.0	72.0*	72.0
Oven temperature °C.....	115.0	114.0	114.0
Coal temperature °C.....	161.0	165.0	138.0
Rise temperature °C.....	46.0	51.0	28.0

*The heat current had been turned off at power house. Coals were left two days longer.

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TABLE 5
SERIES 4—WET COAL—3 PER CENT PYRITE

	Coal 0	Coal 0- $\frac{1}{8}$	Coal $\frac{1}{8}$ - $\frac{1}{4}$
Time in hours.....	72.0	72.0	72.0
Oven temperature °C.....	39.5	40.0	39.5
Coal temperature °C.....	39.5	39.2	42.3
Rise temperature °C.....	0.0	2.8
Time in hours.....	72.0	72.0	72.0
Oven temperature °C.....	60.0	60.0	61.0
Coal temperature °C.....	56.5	55.7	66.5
Rise temperature °C.....	5.5
Time in hours.....	72.0	72.0	72.0
Oven temperature °C.....	80.0	80.0	80.0
Coal temperature °C.....	86.7	82.8	89.8
Rise temperature °C.....	6.7	2.8	9.8
Time in hours.....	72.0	72.0	72.0
Oven temperature °C.....	112.5	115.0	115.0
Coal temperature °C.....	226.2	172.0	126.0
Rise temperature °C.....	113.7*	57.0*	11.0

*Upon removal from the oven and standing at room temperature, the interior of the mass within the jar took fire and after a period of from 2 to 3 weeks was consumed.

TABLE 6
SERIES 5—DRY COAL—5 PER CENT PYRITE

	Coal 0	Coal 0- $\frac{1}{8}$	Coal $\frac{1}{8}$ - $\frac{1}{4}$
Time in hours.....	72.0	72.0	72.0
Oven temperature °C.....	34.0	39.0	40.0
Coal temperature °C.....	38.0	42.4	42.0
Rise temperature °C.....	4.0	3.4	2.0
Time in hours.....	72.0	72.0	72.0
Oven temperature °C.....	60.5	60.3	61.0
Coal temperature °C.....	70.0	66.2	66.6
Rise temperature °C.....	9.5	5.9	5.6
Time in hours.....	*	72.0	72.0
Oven temperature °C.....	80.5	81.0
Coal temperature °C.....	88.2	89.2
Rise temperature °C.....	7.7	8.2
Time in hours.....	72.0	72.0	72.0
Oven temperature °C.....	122.0	120.0	116.0
Coal temperature °C.....	185.0	174.0	143.2
Rise temperature °C.....	63.0	54.0	27.2

*Battery worn out, so regulator did not work; was recharged and put in order.

Series 4.—In Series 4 the conditions of the experiment were precisely as in Series 3, with the exception that the coal was thoroughly wet before placing in the ovens.

Series 5.—In Series 5 the conditions were the same as in Series 1 and 3, with the exception that the content of iron pyrites was increased to 5 per cent.

The first lot of coal being exhausted, a new lot was procured. This was from the same source and was hand-picked as before, but it was deemed advisable to make a careful analysis again. This analysis is shown in the following table.

TABLE 7

	Per cent
Moisture	4.34
Volatile matter	33.38
Fixed carbon	50.25
Ash	12.03
Total	100.00
Sulphur	1.17

Calculated to Dry Coal

Volatile matter	34.89
Fixed carbon	52.43
Ash	12.68
Total	100.00
Sulphur	1.22

The pyritic content of the coal was determined as before. The total iron in the coal was determined, and from it the iron soluble in dilute hydrochloric acid was subtracted; this gave the pyritic iron, and from the latter the pyrite was calculated.

	Per cent
Total iron	1.440
HCl soluble Fe	0.510
Pyritic iron	0.930
Calculated	
Pyrite content	1.397

The iron was determined volumetrically by the Zimmermann-Reinhardt method, as modified by Jones and Jeffery¹.

It will be noted that the pyrite content of the second lot of coal is slightly less than that used in the former series. This fact was taken into account, however, in making up the pyrite content of the coal; the pyrite used was some of the same lot that was used in making up the first 5 series.

Series 6.—In Series 6 the conditions were the same as those maintained in Series 2 and 4, with the exception that the content of iron pyrites was increased to 5 per cent. The mass was thoroughly wet down before the samples were placed in the ovens.

TABLE 8
SERIES 6—WET COAL—5 PER CENT PYRITE

	Coal 0	Coal 0- $\frac{1}{8}$	Coal $\frac{1}{8}$ - $\frac{1}{4}$
Time in hours.....	72.0	72.0	
Oven temperature °C.....	40.0	40.0	
Coal temperature °C.....	41.0	41.0	
Rise temperature °C.....	1.0	1.0	
Time in hours.....	72.0	72.0	72.0
Oven temperature °C.....	62.0	62.0	90.0 ²
Coal temperature °C.....	62.0	64.5	105.0
Rise temperature °C.....	0.0	2.5	15.0
Time in hours.....	72.0	72.0	72.0
Oven temperature °C.....	83.0	83.0	83.0
Coal temperature °C.....	90.0	94.0	91.0
Rise temperature °C.....	7.0	11.0	8.0
Time in hours.....	72.0	72.0	72.0
Oven temperature °C.....	110.5	126.0	116.0
Coal temperature °C.....	210.0 ³	169.0	133.0
Rise temperature °C.....	100.0	43.0	17.0

Series 7.—In Series 7 the content of iron pyrites was left the same as in the natural coal. It was not thought advisable to carry the amount of iron pyrites above the 5 per cent as used in Series 5 and 6, for the reason that a consistent increase in ac-

¹Analyst, Vol. 34, p. 306 (1909).

²Battery run down; was recharged; the coal was again thoroughly wet, as it had dried out.

³210° was as high as the thermometer would register. Upon removal from the oven the coal took fire, as in Series 4.

TABLE 9

SERIES 7—MIXED COAL—DRY AND WET—1.40 PER CENT PYRITE

	Dry	Wet
Time in hours.....	72.0	72.0
Oven temperature °C.....	40.0	40.0
Coal temperature °C.....	44.0	41.0
Rise temperature °C.....	4.0	1.0
Time in hours.....	72.0	72.0
Oven temperature °C.....	62.0	62.0
Coal temperature °C.....	67.5	62.0
Rise temperature °C.....	5.5	0.0
Time in hours.....	72.0	72.0
Oven temperature °C.....	86.0	83.0
Coal temperature °C.....	101.5	89.0
Rise temperature °C.....	15.5	6.0
Time in hours.....	72.0	72.0
Oven temperature °C.....	110.5	110.5
Coal temperature °C.....	128.5	127.5
Rise temperature °C.....	18.0	17.0

TABLE 10

SERIES 8—MIXED COAL—DRY AND WET—3 PER CENT PYRITE

	Dry	Wet
Time in hours.....	72.0	72.0
Oven temperature °C.....	40.0	41.0
Coal temperature °C.....	45.5	44.0
Rise temperature °C.....	5.5	3.0
Time in hours.....	72.0	72.0
Oven temperature °C.....	62.0	62.0
Coal temperature °C.....	67.0	65.5
Rise temperature °C.....	5.0	3.5
Time in hours.....	72.0	72.0
Oven temperature °C.....	83.0	83.0
Coal temperature °C.....	95.0	93.0
Rise temperature °C.....	12.0	10.0
Time in hours.....	72.0	72.0
Oven temperature °C.....	148.0	147.0
Coal temperature °C.....	192.0	198.0
Rise temperature °C.....	44.0	51.0

tivity accompanies the increase of pyrites to 3 per cent, and again to 5 per cent, which seemed ample verification of the principle involved. Moreover, this latter amount approximates the limit of this substance as actually found in coals of this region. However, the variable employed in this series was the fact that sizing of the coal was not carried out. The lump material was passed through a small Chipmunk jaw crusher, set to deliver the coal in pieces not exceeding $\frac{1}{4}$ in. to $\frac{1}{2}$ in. in diameter, but carrying with it a very considerable amount of dust and fine particles. Since this plan involved the use of but one sample to cover the mixture of sizes, the dry and wet mixtures were carried along parallel and are covered in the table for Series 7.

Series 8.—In Series 8 the sample of coal was prepared exactly as in Series 7, with the exception that the content of pyrites was increased to 3 per cent. Parallel jars of wet and dry coal were carried through the series as in 7.

Series 9.—In Series 9 the conditions were the same as in Series 7 and 8, with the exception that the content of pyrites was increased to 5 per cent. Parallel samples of wet and dry material were carried through as before.

TABLE 11

SERIES 9—MIXED COAL—DRY AND WET—5 PER CENT PYRITE

	Dry	Wet
Time in hours.....	72.0	72.0
Oven temperature °C.....	41.0	40.0
Coal temperature °C.....	47.0	40.0
Rise temperature °C.....	6.0	0.0
Time in hours.....	72.0	72.0
Oven temperature °C.....	62.0	62.0
Coal temperature °C.....	68.0	65.0
Rise temperature °C.....	6.0	3.0
Time in hours.....	72.0	72.0
Oven temperature °C.....	83.0	83.0
Coal temperature °C.....	95.0	93.0
Rise temperature °C.....	12.0	10.0
Time in hours.....	72.0	72.0
Oven temperature °C.....	142.0	132.0
Coal temperature °C.....	186.0	180.0
Rise temperature °C.....	44.0	48.0

Series 10.—In the foregoing series, the evidence was conclusive to the effect that with the finer sizes and the presence of iron pyrites of 3 per cent or over, together with moisture, there resulted a rise in temperature which quickly resulted, upon removal to the air, in combustion of the coal. This property was marked in both the 0 size and the $0\text{--}\frac{1}{8}$ in. size and, since the latter was easy to prepare, it was made use of in the subsequent experiments, together with 5 per cent pyrites, for the purpose of testing the effect of various salt solutions as a possible means of checking the rise in temperature.

In Series 10, two strengths of sodium chloride solution were used with results as shown in Table 12.

TABLE 12

SERIES 10—SIZE $0\text{--}\frac{1}{8}$ —5 PER CENT PYRITE

	Wet with 3 per cent NaCl Solution	Wet with 10 per cent NaCl Solution
Time in hours.....	72.0	72.0
Oven temperature °C.....	43.0	43.0
Coal temperature °C.....	43.0	43.0
Rise temperature °C.....	0.0	0.0
Time in hours.....	72.0	72.0
Oven temperature °C.....	63.0	63.0
Coal temperature °C.....	63.0	62.0
Rise temperature °C.....	0.0	
Time in hours.....	72.0	72.0
Oven temperature °C.....	83.0	82.0
Coal temperature °C.....	89.0	88.0
Rise temperature °C.....	6.0	6.0
Time in hours.....	72.0	72.0
Oven temperature °C.....	112.0	115.0
Coal temperature °C.....	180.0	190.0
Rise temperature °C.....	68.0	75.0

Series 11—In Series 11 the same conditions were maintained as in Series 10, with the exception that 3 per cent and 10 per cent solutions, respectively, of calcium chloride were employed.

TABLE 13
SERIES 11—SIZE 0- $\frac{1}{8}$ —5 PER CENT PYRITE

	Wet with 3 per cent CaCl ₂ Solution	Wet with 10 per cent CaCl ₂ Solution
Time in hours.....	72.0	72.0
Oven temperature °C.....	43.0	43.0
Coal temperature °C.....	42.0	43.0
Rise temperature °C.....	0.0
Time in hours.....	72.0	72.0
Oven temperature °C.....	63.0	63.0
Coal temperature °C.....	63.0	63.0
Rise temperature °C.....	0.0	0.0
Time in hours.....	72.0	72.0
Oven temperature °C.....	82.0	83.0
Coal temperature °C.....	91.0	85.0
Rise temperature °C.....	9.0	2.0
Time in hours.....	72.0	72.0
Oven temperature °C.....	124.0	122.0
Coal temperature °C.....	184.0	148.0
Rise temperature °C.....	60.0	26.0

TABLE 14
SERIES 12—SIZE 0- $\frac{1}{8}$ —5 PER CENT PYRITE

	Wet with Saturated Lime Water
Time in hours.....	72.0
Oven temperature °C.....	43.0
Coal temperature °C.....	43.0
Rise temperature °C.....	0.0
Time in hours.....	72.0
Oven temperature °C.....	63.0
Coal temperature °C.....	63.0
Rise temperature °C.....	0.0
Time in hours.....	72.0
Oven temperature °C.....	83.0
Coal temperature °C.....	91.0
Rise temperature °C.....	8.0
Time in hours.....	72.0
Oven temperature °C.....	124.0
Coal temperature °C.....	168.0
Rise temperature °C.....	44.0

TABLE 15

SERIES 13—SIZE 0- $\frac{1}{8}$ —5 PER CENT PYRITE

	Wet with 3 per cent NaHCO_3 Solution	Wet with 10 per cent NaHCO_3 Solution
Time in hours.....	72.0	72.0
Oven temperature °C.....	43.0	43.0
Coal temperature °C.....	43.0	43.0
Rise temperature °C.....	0.0	0.0
Time in hours.....	72.0	72.0
Oven temperature °C.....	63.0	63.0
Coal temperature °C.....	63.0	63.0
Rise temperature °C.....	0.0	0.0
Time in hours.....	72.0	72.0
Oven temperature °C.....	83.0	83.0
Coal temperature °C.....	93.0	92.0
Rise temperature °C.....	10.0	9.0
Time in hours.....	72.0	72.0
Oven temperature °C.....	126.0	123.0
Coal temperature °C.....	174.0	161.0
Rise temperature °C.....	48.0	38.0

TABLE 16

SERIES 14—SIZE 0- $\frac{1}{8}$ —5 PER CENT PYRITE

	Wet with 3 per cent FeSO_4 Solution	Wet with 10 per cent FeSO_4 Solution
Time in hours.....	72.0	72.0
Oven temperature °C.....	43.0	43.0
Coal temperature °C.....	43.0	43.0
Rise temperature °C.....	0.0	0.0
Time in hours.....	72.0	72.0
Oven temperature °C.....	63.0	63.0
Coal temperature °C.....	63.0	63.0
Rise temperature °C.....	0.0	0.0
Time in hours.....	72.0	72.0
Oven temperature °C.....	83.0	83.0
Coal temperature °C.....	93.0	95.0
Rise temperature °C.....	10.0	12.0
Time in hours.....	72.0	72.0
Oven temperature °C.....	132.0	124.0
Coal temperature °C.....	181.0	186.0
Rise temperature °C.....	49.0	62.0

Series 12.—In Series 12 the same conditions as to size and pyritic content were maintained, the wetting of the coal being accomplished with a saturated solution of lime water.

Series 13.—The same size of coal with the same pyritic content was employed as in Series 10–13 inclusive, excepting that the solutions used were 3 per cent and 10 per cent respectively, of sodium bicarbonate.

Series 14.—In Series 14 the conditions as to size and pyritic content were maintained as in Series 10–13 inclusive. The solutions employed, however, were 3 per cent and 10 per cent of sulphate of iron.

Series 15.—In Series 15 the principle employed was that of subjecting the sample to pre-heating at temperatures approaching the extremes attained in the ovens under the several series preceding. This series was made up as follows:

One jar of size 0– $\frac{1}{8}$, 5 per cent pyrite, dry.

One jar of mixed coal, i. e., a mixture of about equal parts of sizes, 0– $\frac{1}{8}$, $\frac{1}{8}$ – $\frac{1}{4}$, $\frac{1}{4}$ – $\frac{3}{8}$, and $\frac{3}{8}$ – $\frac{1}{2}$, made up to 5 per cent pyrite, dry.

One jar of exceedingly fine coal, finer than ordinary dust, made by grinding the coal for 100 hours in a ball mill, the latter being a large iron jar with a porcelain lining, having a screw cover. About equal parts of coal and 1 in. to $1\frac{1}{2}$ in. quartz pebbles were put into the jar. After grinding, the coal was sifted through a 200-mesh sieve so as to remove any small lumps, and was then made up to 5 per cent pyrite, dry.

These three jars of coal were placed in the 40° oven first and moved up after 3 days, as described previously. After being taken from the 115°–120° oven, they were allowed to cool for 3 days and then were replaced in the oven for 3 days, the rise in temperature in all cases being noted.

TABLE 17
SERIES 15
First Heating

	Mixed Coal
Time in hours.....	72.0
Oven temperature °C.....	120.0
Coal temperature °C.....	163.0
Rise temperature °C.....	43.0

Second Heating

Time in hours.....	72.0
Oven temperature °C.....	135.0
Coal temperature °C.....	146.0
Rise temperature °C.....	11.0

First Heating

	Size 0- $\frac{1}{8}$
Time in hours.....	72.0
Oven temperature °C.....	140.0
Coal temperature °C.....	210.0
Rise temperature °C.....	70.0

Second Heating

Time in hours.....	72.0
Oven temperature °C.....	136.0
Coal temperature °C.....	155.0
Rise temperature °C.....	19.0

First Heating

	Ball Mill Size
Time in hours.....	48.0
Oven temperature °C.....	69.0
Coal temperature °C.....	205.0
Rise temperature °C.....	136.0

Second Heating

Time in hours....	72.0
Oven temperature °C.....	64.0
Coal temperature °C.....	73.0
Rise temperature °C.....	9.0

Third Heating

Time in hours.....	72.0
Oven temperature °C.....	147.0
Coal temperature °C.....	220.0
Rise temperature °C.....	73.0

III. DISCUSSION OF RESULTS

DISCUSSION AND PRESENTATION OF DATA

Series 1.—In order to make possible a more critical and comparative study of the various series, the temperature increases as tabulated in Series 1 to 15 were plotted in the form of curves, in which the oven temperatures were taken as the abscissas, and the rise over the oven temperatures as the ordinates. These curves shows many interesting results, and a detailed study can be more advantageously made by reference to the curves rather than to the temperature tables.

Fig. 3 shows that the temperature increase is greater as the size of the coal decreases and that most of the oxidation, assuming it may be measured by the rise in temperature, takes place above 60°C., with a more positive index of activity than at 80°. In examining these details of oxidation and the accompanying temperatures, it is very suggestive to review briefly the studies

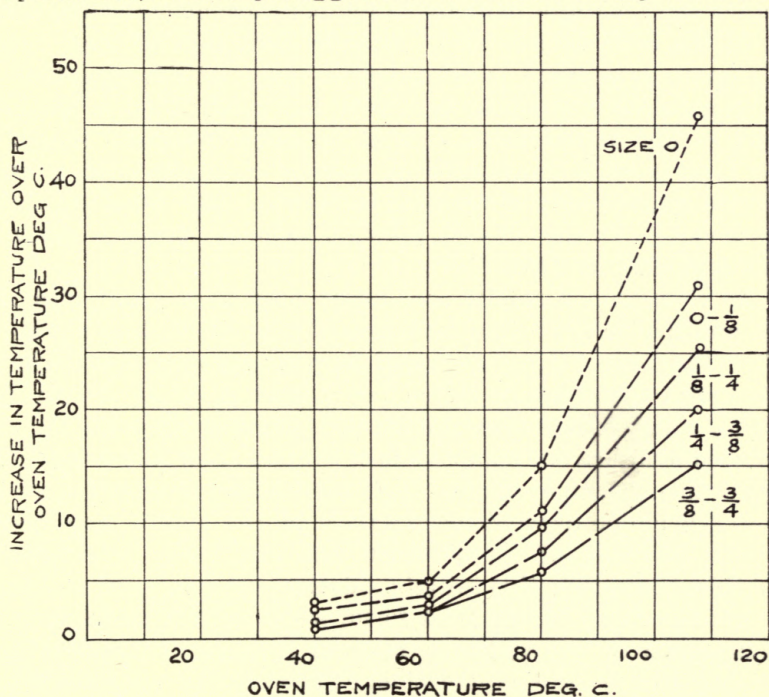


FIG. 3.
SERIES 1—1.65% PYRITE—DRY COAL.

on oxidation temperatures as carried out by Parr and Francis.¹ Those studies were conducted upon 2-gram samples of coal, suspended in an atmosphere of oxygen, with one thermometer for reading the temperature of the coal and another for indicating the temperature of the surrounding gas. In addition to the temperature rise of the coal, the appearance of carbon dioxide in the circulating gas served as an index of the starting and to some extent of the oxidation. In these previous experiments, the observed point where carbon dioxide appeared in the escaping gas was, in general, from 112°C. to 125°C., and the oxidation became so active as to show a marked increase in the internal coal temperature. From this point onward, the conditions for arriving at active combustion were quickly reached. Comparing these facts with those indicated by the curves in Fig. 3 we see a striking suggestion of chemical action other than that which results in the formation of CO₂. For example, at 80° in Fig. 3, all of the samples show a slight increase in temperature over the temperature of the oven atmosphere. It is evident that in these large 40-lb. samples a much more sensitive index of the inception of heat generation is obtained than with the small 2-gram samples of the earlier experiments, so that doubtless chemical action in some form must be considered as having commenced at a temperature considerably lower than the 110° to 120° shown in those experiments. In the present tests, it assumes positive activity quite uniformly at about 80°C.

An element not usually considered may here enter into the case, and that is the initial oxidation of coal which does not show itself in the form of CO₂. Parr and Barker² and also Chamberlain³ have shown that freshly mined coals have a great avidity for oxygen, which enters into combination presumably with the unsaturated hydrocarbon compounds of the coal, and this action goes on at ordinary temperatures. Just what heat increment may be due to this action or what acceleration of the action may result from an increase of temperature has not been investigated. Doubtless, however, this initial oxidation extends over and merges into the more pronounced form, which shows itself both in the presence of CO₂ and in a marked increase in temperature. This may be a partial explanation, at least for the peculiarity of

¹ Bulletin No. 24, U. of I., Eng. Exp. Sta., June, 1908.

² Bulletin No. 32, U. of I., Eng. Exp. Sta., March, 1909.

³ Bulletin No. 383, U. S. G. S., 1909.

the curve in Fig. 6 of Series 3. A still more noticeable suggestion of the earlier studies on oxidation is found in the higher temperatures. For example, with the oven temperature at 108° , these larger coal masses have attained temperatures ranging from 115° to 145° , and from this latter point, the progress to ignition temperatures as indicated in the earlier tests on the small samples would be very rapid. This was found to be the case, as will be seen from a study of the subsequent experiments.

Series 2.—From the curves of Series 2, Fig. 4, it may be seen, as expected, that any heat generated by the process of oxidation is used in driving off the water with which the coal was thoroughly soaked before putting in the ovens. At 80° C., however, we get an increase in temperature over the oven temperature, even though the coal still contains some moisture. It is to be noticed, however, that the final increase in temperature of the two finer sizes is somewhat greater than in Series 1, when the same coal was used dry.

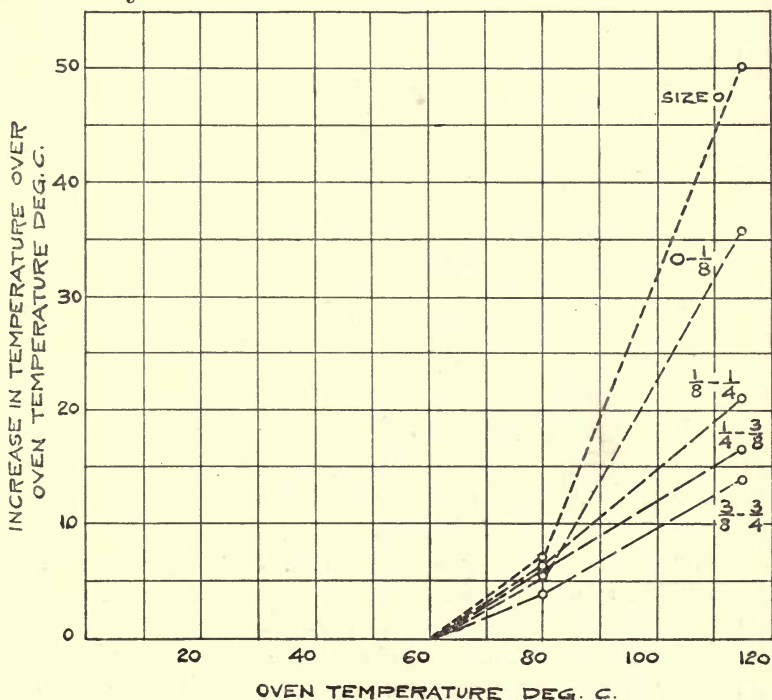


FIG. 4.

SERIES 2—1.65% PYRITE—WET COAL.

Series 3. — Fig. 5, giving the results of Series 3, shows a new and interesting phenomenon, viz., the effect of the size of the coal on the rate of oxidation. Series 1 showed that the fine coals oxidize more than coarse sizes, and also gave an indication of the rate of oxidation, although this was not noticed in time to make a detailed study of it in the first series. In Series 3, however, temperature readings were made every few hours during the time that size 0 was in the 115° – 120° oven. As is seen in Fig. 5,

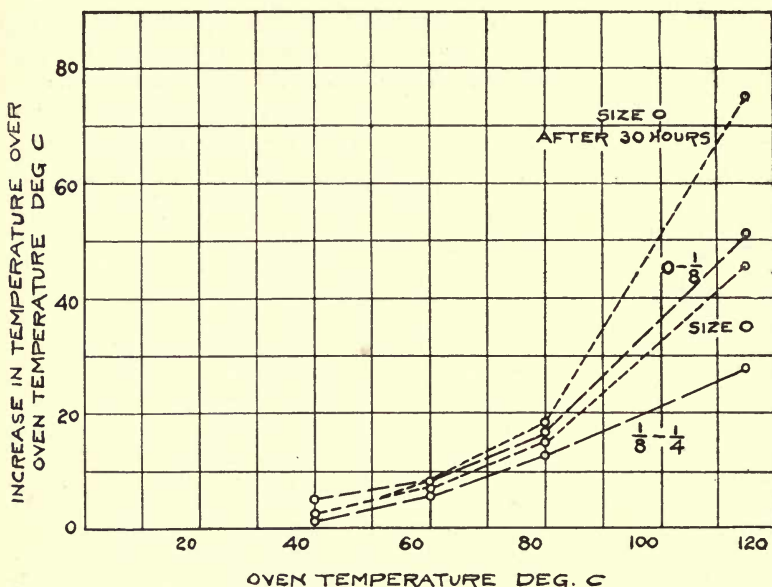


FIG. 5.
SERIES 3—3% PYRITE—DRY COAL.

the curve of size 0 is made up of two curves, one of which rises to an excess temperature of 75.3° and the other shows an increase of 46° , which is even lower than the temperature increase of the next size, which is 51° . The first temperature of 75.3° was reached after the coal had been in the oven only 30 hours, and from that time until the end of the 72 hours, the temperature gradually decreased to 46° , which was the final temperature. The results of this study of the rate of oxidation, as measured by the increase of the coal temperature over the oven temperature is shown in graphical form in Fig. 6.

As seen from this curve the temperature increased very rapidly during the first 30 hours, when it reached a maximum, and it is very probable that at this point this fine size of coal had saturated itself with oxygen. The temperature then gradually decreased until the final temperature was only a little more than one-half the maximum temperature attained. This phenomenon was observed only in the case of the finest size, size 0; the rise in temperature of the coarser sizes was a gradual rise over the entire period of 72 hours. If an average between the maximum and final temperature of size 0 is taken, then a consistent, though not very marked rise in temperature of Series 3 over Series 1, is noticed. These two series are the same throughout, excepting their pyrite content.

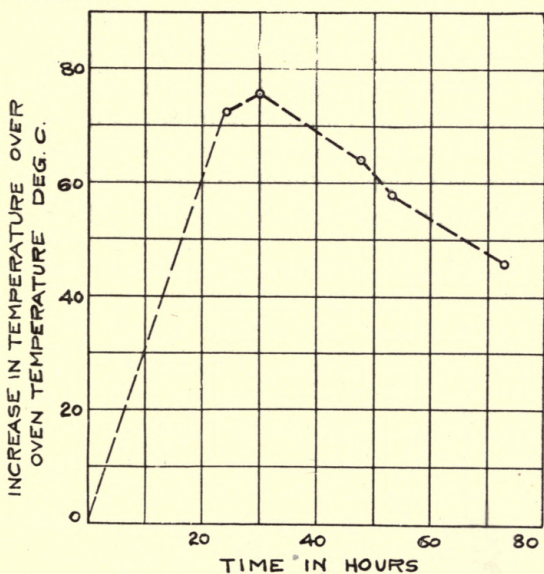


FIG. 6.

SERIES 3—3% PYRITE—SIZE 0—DRY COAL.

Series 4.—Series 4 was coal having the same pyrite content as the preceding series, only in this case the coal was first thoroughly wet. Several new points are seen. Size $\frac{1}{8}$ – $\frac{1}{4}$, which was as dust free as it was possible to make it, dried out very soon and showed an increase in temperature even in the 40° and 60° ovens, whereas the two finer sizes did not even get dry at these temperatures. Size 0, at the end of three days, showed an increase over the oven temperature, of 113.7°, this being as high as the thermome-

ters would register. On removal from the oven and on examination the following day, it was found that the coal had taken fire and that the thermometer was not far enough down in the coal to measure the total increase in temperature. The coal took fire in the middle of the jar, and, because of the slight access of air, the burning was only a slow smoldering. The jar was left out in the room temperature for about two weeks after it was taken from the oven, and was then re-examined. It was found that the coal on the interior of the jar had burned completely to an ash, although there was a ring of unburned coal all around the inside of the jar about 3 in. thick. This ring of unburned coal probably acted as an insulator for the burning coal within the jar, for being at room temperature, the coal nearest the sides of the jar was at too low a temperature to burn. After removing size 0- $\frac{1}{8}$ from the ovens it was allowed to stand in the container for several weeks, when it was found that it also had started to burn, although the combustion was not as complete as in the former case, and although the rise in temperature while in the ovens was not any greater than had been attained by some of the dry coals which had not taken fire under similar conditions. This series shows,

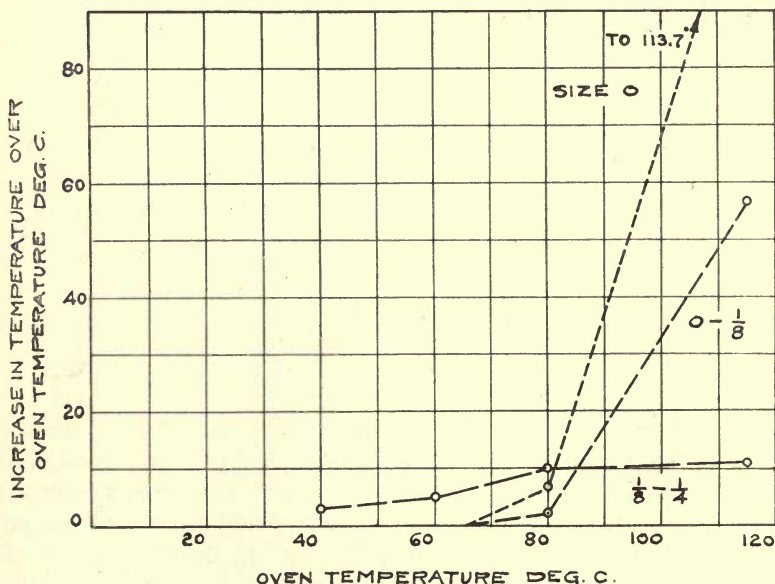


FIG. 7.
 SERIES 4—3% PYRITE—WET COAL.

therefore, the effect of having the coal wet and also shows how much more dangerous and how much greater is the liability of a coal to ignite spontaneously if it has been wet. The fact that the coal in this series took fire and that the coal in the preceding series which was of the same composition did not, shows the significance and danger arising from a coal, dependent entirely upon its condition when stored.

Attention is here directed again to the former studies on oxidation by Parr and Francis¹. In that work it was found that up to a certain point, oxidation continued only so long as the external source of heat continued, but after that point was passed, the oxidation was self-propelling, passing very quickly to the ignition stage. In the powdered sizes and in an atmosphere of oxygen, this rapid oxidation began quite uniformly at about 160°C., and soon thereafter ran up rapidly to ignition. In air, a temperature above 200° was required. This phenomenon is practically duplicated in Series 4, where the zero size of coal, after reaching 193° within the oven, had sufficient elevation to continue in its chemical activity to the ignition point upon being set out into the open air, and thus completed the demonstration of actual burning up of the sample.

Series 5.—Series 5 shows a slightly greater rise in temperature than does Series 3, and, since these two series were exactly the same in all respects except the pyrite content, it seems reasonable to suppose that the greater degree of oxidation, as measured by the rise in temperature, of Series 5 over Series 3 must be attributed in some way to the increased amount of pyrite present. It is true that the increase of temperature rise of Series 5 over Series 3 is not very great, but it is consistent in all the sizes, and as the pyrite content was the only variable in the two systems, the possibility of other factors causing an increase in temperature seems to be excluded.

Series 6.—Series 6 tends to confirm the results obtained in Series 4 in that size 0 again took fire, although size 0- $\frac{1}{8}$ in Series 6 did not show signs of active combustion as did the same size in Series 4; still it sintered together to form a cake, and in all probability would have taken fire had it been allowed to remain in the oven a little while longer. This difference in action of these two

¹ Bulletin No. 24, U. of I., Eng. Exp. Sta., June, 1908.

sizes in the wet series may be accounted for by the fact that size 0- $\frac{1}{8}$ in Series 6 may have had a little more water in it than the same size in Series 4, and, so may have taken a little longer time to dry

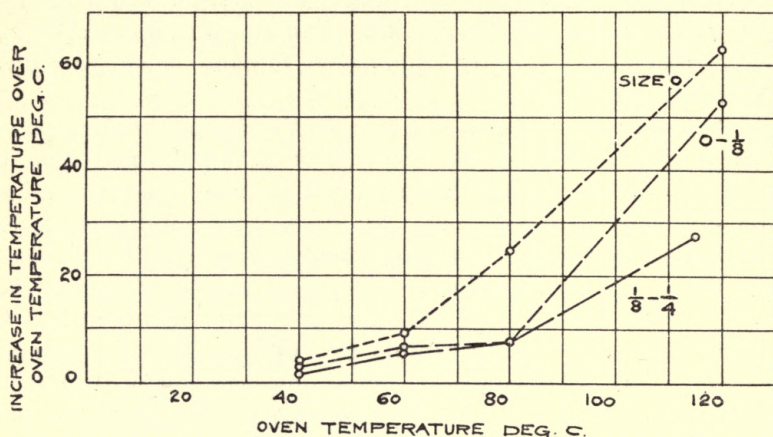


FIG. 8.

SERIES 5—5% PYRITE—DRY COAL.

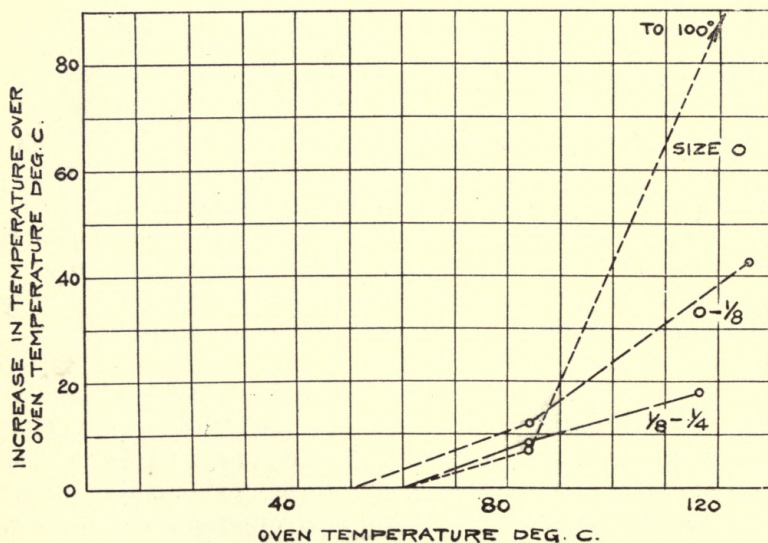


FIG. 9.

SERIES 6—5% PYRITE—WET COAL.

out, thus being in the oven a shorter length of time after it had become dry. For each size an attempt was made to use practically the same amount of water, and in the finer sizes this usually required between four and five liters. In wetting the coal, the water was added slowly with continual stirring, so as to drive out all the air, and the wet coal then had the consistency of a thick slush. The fact that the finest size of Series 4 and 6 took fire, while of the same size and having the same composition, the only difference being that the coal was dry, (Series 3 and 5), did not fire, certainly seems to prove the statements made on page 28 concerning the results of Series 4.

OXIDATION OF SULPHUR AND RESULTING HEAT INCREMENT

To determine how great an oxidation of pyrite took place, the water-soluble sulphur in the fresh coal and the various sizes of oxidized coal was determined. This was done only in Series 2, 4, and 6, where the coal had been wet, for it was thought that the oxidation of the dry pyrite would not be very great. The results are:

Water-Soluble sulphur in the fresh coal...0.0189 per cent.

Water-Soluble sulphur in the oxidized coal:

	Size 0 percent	0- $\frac{1}{8}$ percent	$\frac{1}{8}$ - $\frac{1}{4}$ percent	$\frac{1}{4}$ - $\frac{3}{8}$ percent	$\frac{3}{8}$ - $\frac{1}{2}$ percent
Series 2.....	0.196	0.178	0.0317	0.0231	0.0214
Series 4.....	0.349	0.340	0.1088		
Series 6.....	0.744	0.698	0.5520		

Deducting the 0.0189 per cent of water-soluble sulphur originally present in the coal, occurs, as the result of the oxidation:

	Size 0 percent	0- $\frac{1}{8}$ percent	$\frac{1}{8}$ - $\frac{1}{4}$ percent	$\frac{1}{4}$ - $\frac{3}{8}$ percent	$\frac{3}{8}$ - $\frac{1}{2}$ percent
Series 2.....	0.177	0.159	0.0298	0.0212	0.0195
Series 4.....	0.330	0.321	0.0999		
Series 6.....	0.725	0.679	0.5330		

If we average the water-soluble sulphur of the two finest sizes, (the coarse dust-free sizes of coal did not retain much of the finely ground added pyrite), and calculate the water-soluble sulphur to pyrite, then we can get a fair estimate of the amount of pyrite that has been oxidized to the soluble ferrous sulphate condition.

	Original Pyrite Content per cent	H ₂ O Soluble S per cent	H ₂ O Solu- ble S Calcu- lated to FeS ₂ per cent	Ratio of Calcu- lated FeS ₂ to Original per cent
Series 2.....	1.65	0.168	0.308	18.7
Series 4.....	3.00	0.326	0.612	20.4
Series 6.....	5.00	0.702	1.316	18.8

From the above table, it may be seen that even with widely differing pyritic contents, the amount oxidized was practically constant, for, as shown in the last column of the above table, about 19 per cent of the pyrite present in the coal was oxidized to a soluble condition.

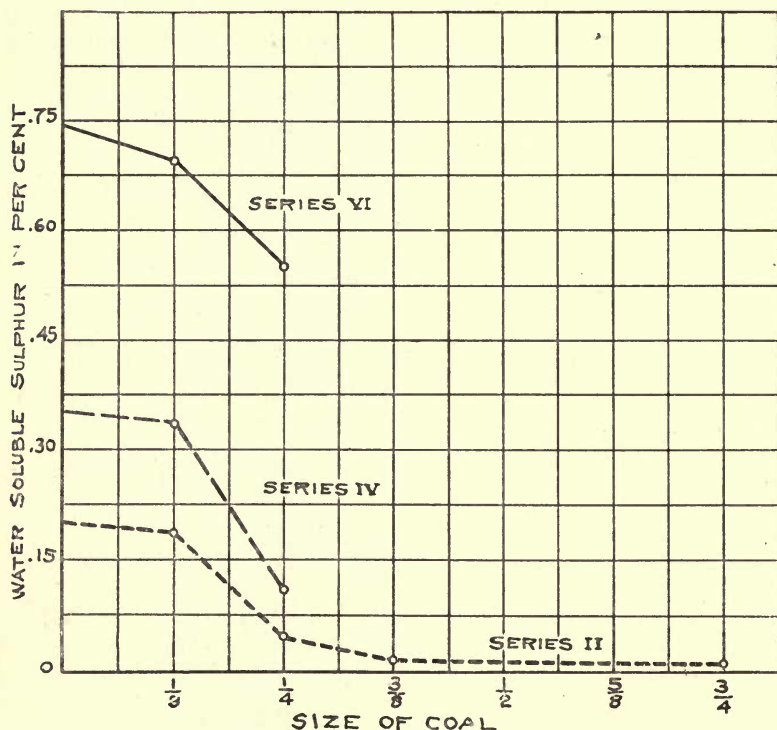
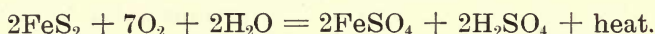


FIG. 10.

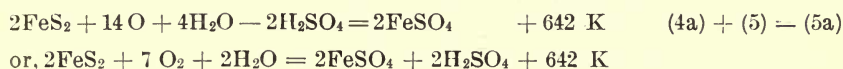
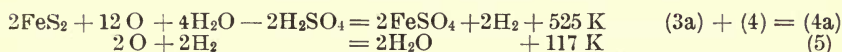
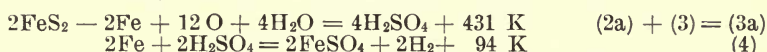
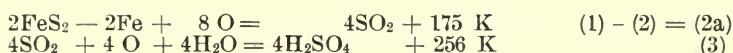
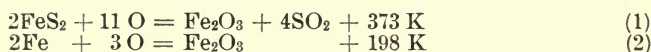
SERIES 2—1.65% PYRITE—WET COAL. SERIES 4— 3% PYRITE—WET COAL.
SERIES 6— 5% PYRITE—WET COAL.

Having determined the degree of oxidation of the pyrite, it would be interesting to learn how great an increase in temperature would be due to the heat liberated by the oxidation of the pyrite, without taking into consideration the heat liberated by

the absorption of oxygen by the carbonaceous material. Pyrite oxidizes according to the following equation:



It is true that the oxidation goes further: the final product is probably a mixture of ferric sulphate ($\text{Fe}_2(\text{SO}_4)_3$) and basic ferric sulphate ($\text{Fe}(\text{OH})\text{SO}_4$), and this would tend to increase the amount of heat liberated. Also, some of the free sulphuric acid formed would combine with some of the basic materials present in the coal, such as lime or alkali, but for the sake of simplicity and to be sure of obtaining a conservative or rather a minimum estimate of the effect of this heat, only the heat liberated in the above reaction was calculated. The data of the heat of formation of the oxidation of pyrite to ferrous sulphate are not yet known; at least a record could not be found in any of the standard physical-chemical authorities, but Somermeier¹ has determined the heat of combustion of pyrite to ferric oxide and sulphur dioxide, so by calculation involving known reactions, the heat liberated in the above equation is found as follows:



K is used as the symbol for the large calorie, the heat liberated in each of the above equations being expressed in mols of the substance in the reactions. No account is made in this calculation of the heat of solution of the sulphuric acid nor of the hydration of the ferrous sulphate. If the weight of a jar of coal be assumed as 40 lb., (18.12 kilograms), and if the coal contains 5 per cent of pyrite, then it will contain 2 lb. (906 grams), of pyrite. The latter is 19.3 per cent oxidized, then 19.3 per cent of 906 grams will

¹Jour. of the Am. Chem. Soc., Vol. 26, p. 566.

NOTE.—He finds that 1 gram of sulphur in the form of FeS_2 yields 2915 calories. Then, 2 gram-mols of FeS_2 would yield $2915 \times .533 \times 240 = 373$ large calories.

enter into the reaction (or 177 grams). The molecular weight of pyrite is 120, and two molecules entering into the reaction would be 240, hence $\frac{177}{240} \times 642$ K, or 473 K will be obtained as the heat liberated by the oxidized pyrite in 40 lb. of coal. The specific heat of the coal used is not known, but some rough experiments by Threlfall¹ show that the specific heat of bituminous coal varies from 0.3 to 0.45, with the average at about 0.35. If the specific heat of the coal used be assumed as 0.35, then the heat generated by the oxidation of the pyrite would be sufficient to raise the temperature of the coal

$\frac{473}{18.12 \times .35}$ or 74.5° , which, it may be seen, is sufficient in amount to account for the larger part of the increase as indicated by the curves. Threlfall calculated the heat of oxidation of pyrite from one of Richter's experiments, the data of which were available. He also calculated the heat of oxidation of the carbonaceous material from the loss of hydrogen and carbon during the oxidation. In this experiment, the coal was heated to a temperature of 190°C . for ten hours in a slow stream of air. The oxidation of the pyrite gave enough heat to give a rise in temperature of 175° , and the oxidation due to absorption of the oxygen gave a rise of 750° , about four times as much. From these data, the total heat evolved from the pyritic oxidation does not seem important when compared with the heat liberated by the absorption of oxygen, but it is to be remembered that the absorption of oxygen by coal is immensely accelerated at an increased temperature, and it seems very probable that the pyritic oxidation may be the means by which this temperature, favorable to active oxygen absorption, is attained.

As has been shown by the work of Parr and Francis,² the temperature at which oxidation of the coal substance itself actually begins (about 120° in oxygen and 135° in air) is comparatively low, and therefore any influence which would serve as a force to bring the coal up to this temperature should be taken into account. Since coal is a rather poor conductor of heat the major part of the heat generated within the pile will be retained, and from the calculation of the heat generated by the pyritic oxidation, it may be seen that a sufficient quantity of heat

¹ Jour. of the Soc. of Chem. Ind., Vol. 28, p. 763.

² Engineering Experiment Station, University of Illinois, Bulletin No. 24.

was liberated to bring the coal up to this temperature of 135° , at which active oxidation of the carbonaceous materials begins. Of course the rise in temperature of a coal pile in storage up to 135° should not be ascribed to the effect of the pyritic oxidation alone, for it is the result of the heat liberated by the oxidation of both the coal and the pyrite. The above, however, was merely given as an example to show how great the effect of the pyritic oxidation may be.

Since the above experiments show that the oxidation of the pyrite is practically constant, that is, about one-fifth of the total pyrite present, then it follows that coals with increasing pyrite contents will have a corresponding increase in pyritic oxidation and a correspondingly greater amount of heat will be liberated. The result is a hastening of the rise in temperature up to the critical point at which the absorption of oxygen by the coal itself is rapid enough to increase the temperature up to the point of self ignition. This seems to be the explanation of the ignition of Series 4 and 6 which were identical in composition, size, and method of treatment with Series 2, except that the former contained a quantity of pyrite sufficient to cause the coal to ignite, whereas in the latter series the quantity of pyrite present was not great enough to cause this initial rise in temperature up to the critical point at which no external impetus is necessary.

It is to be remembered, of course, that in actual storage the pyritic oxidation will proceed much further than one-fifth of the total pyrite present, as in these particular experiments, but the fact still remains that the degree of pyritic oxidation in coals of various pyrite content is in direct proportion to the pyrite content so long as similar conditions of storage are maintained. It is true, certain coals containing practically no pyrite ignite spontaneously, although from the above work it is reasonable to suppose that an increased amount of pyrite would hasten the ignition. Again, the particular coal worked with did not ignite spontaneously under any conditions until the pyrite content was increased.

It seems, therefore, that the presence of pyrite is a much more important factor in the spontaneous ignition of coal than has heretofore been ascribed to it, and its influence on the spontaneous combustion of coal cannot be discarded in the off-hand way that has been so common with some of the previous investigators, merely because of the fact that some coals containing no pyrite at all would ignite spontaneously.

DETAIL OF ANALYTICAL PROCESSES FOR OXIDIZED SULPHUR

Knowing that Illinois coal contains more or less calcium sulphate, which would partly go into solution and be included in the water-soluble sulphur, it was decided to determine the ferrous sulphate actually present in the fresh coal and also the other sulphur compounds. This necessitated a complete analysis of the ash of the coal, and with the exception of the determination of the alkalis and chlorine, this analysis was made. From other analytical work on coal done in this laboratory it is known that chlorine and sodium and potassium exist in small quantities in the coal, but as the amount of chlorine present is such as to practically neutralize the alkali and, since their presence has no direct bearing upon the work at hand, these constituents were not determined.

For the analysis of the ash, two samples of 10 grams each of coal were used. These were ashed in a platinum dish, then sodium carbonate was added and the fusion completed. The fusion was put in a casserole and dissolved in boiling water, acidified with hydrochloric acid and dehydrated. The analysis was then carried out in the same manner as for any exact silicate rock analysis, with two dehydrations, volatilization of the silica with hydrofluoric acid, etc.

For the determination of iron and aluminum, the filtrate from the above,—along with the residue from the silica determination, which had been fused with potassium pyrosulphate was made alkaline with ammonia. The precipitate of the mixed hydroxides was thoroughly washed and then redissolved in hydrochloric acid, and then was made up to 250 c. c. In 50 c. c. of this solution, the iron was determined volumetrically by the Zimmermann-Reinhardt method. The other 200 c. c. were then reprecipitated with ammonia and weighed.

The calcium was determined by precipitating it as the oxalate, dissolving in sulphuric acid and then titrating with standard potassium permanganate. The magnesium was determined as the pyrophosphate. Since many of the Illinois coals also contain some calcium and magnesium carbonates, the carbon dioxide liberated from the coal by means of boiling 1:2 sulphuric acid was determined in the improved form of the Parr total carbon apparatus¹.

¹ Eng. Exp. Sta. Uni. of Ill., Bull. No. 37 shows diagram of the apparatus.

The results of the above analyses calculated in per cent of the original air-dry coal are as follows:

	Per cent	Per cent
Silica (SiO_2).....	6.108	6.055
Ferric Oxide (Fe_2O_3).....	1.432	1.477
Aluminum Oxide (Al_2O_3 also any P_2O_5 and TiO_2)....	2.108	2.223
Calcium Oxide (CaO)	1.576	1.571
Magnesium Oxide (MgO)	0.123	0.117
Carbon Dioxide (CO_2).....	0.876	0.851

Numerous methods for the determination of the water-soluble iron, that is, iron in ferrous sulphate, were tried. Among these might be mentioned, digesting the coal with water both hot and cold for a period of one or two hours and also over night, using dilute hydrochloric and sulphuric acid in concentrations varying from two drops per 300 c. c. H_2O up to as high as 2 per cent acid. All these methods, however gave discordant and unreliable results.

The method finally adopted, which seemed to give the best results and which minimized the possibility of oxidation, was as follows: Three samples of 25 grams of finely ground air-dry coal were placed in large folded filter papers. About 600 c. c. of well boiled distilled water, which was practically free from air and carbon dioxide, was poured over each sample, the latter being well stirred so as to wet the fine coal thoroughly. The filtrate was then poured back over the coal, and the next filtrate, consisting of the same water as first used, was again poured back on the coal, thus making three leachings with the same water. The coal was finally washed with an additional 100 c. c. of boiling water and the total filtrate then brought to boiling. Five drops of stannous chloride solution were added, the liquid was chilled, an excess of mercuric chloride was added, and in five minutes the mixture was titrated with potassium permanganate. A blank of an equal amount of boiling, distilled water was run through the same procedure. The three titrations, which were made from a burette calibrated by the Reichsanstalt, and which was used for all volumetric work, varied 0.13 c. c. from the lowest to the highest. The results calculated to per cent of air-dry coal were:

0.0059 per cent Fe=0.0160 per cent FeSO_4 =0.0034 per cent S. The water-soluble sulphur directly determined was equal to 0.0189 per cent, and as calculated above from the water-soluble iron was 0.0034 per cent. The difference of these two values 0.0189—0.0034 or 0.0155 per cent is some form of water soluble sulphur other than ferrous sulphate.

The next step was to determine the calcium sulphate present. This was attempted in three ways: first, since one part of calcium sulphate is soluble in about 500 parts of water, it was decided to dissolve out the CaSO_4 by digesting the coal with a large volume of water; second: the calcium sulphate was changed to calcium carbonate and sodium sulphate by the addition of sodium carbonate; and third, since gypsum is soluble in hydrochloric acid, a 10 per cent solution of the latter was added to the coal.

Duplicate samples of 25 grams each of coal were treated as outlined above and were put on the water bath over night. The next day they were filtered and the sulphur carefully precipitated with barium chloride after the filtrates had been concentrated. The results of the six determinations are as follows:

First Method Boiling Water	Second Method 2 per cent Na_2CO_3 Solution	Third Method 10 per cent HCl
0.0192 per cent S 0.0187 per cent S	0.0569 per cent S 0.0571 per cent S	0.0373 per cent S 0.0211 per cent S

The third method with its large variation may be discarded at once, for it seems that the solubility of the gypsum in the acid is not exact or reliable. The first method gave concordant results, but as compared with the second method they are much too low. It is very probable that after a long period of digestion the first and third methods would both give all of the CaSO_4 present, but as the data show, 10 hours' digestion at 100° is not sufficient. The second method gives results probably as nearly correct as can be obtained, although the solubility of calcium carbonate, which is about 50 parts in a million, would create a slight error. The sulphur obtained by the second method (as it would be from any of the three methods outlined) is, therefore, the sulphur from the ferrous and calcium sulphates. The sulphur in the ferrous sulphate, however, was determined by calculation from the water-soluble iron. The difference between these two values would,

therefore, give us the sulphur present as calcium sulphate.
Tabulating these results, we have:

	Per cent	
H ₂ O soluble S calculated from H ₂ O soluble Fe	0.0034	
H ₂ O soluble S directly determined	0.0189	
H ₂ O soluble S plus S in CaSO ₄ (Na ₂ CO ₃ method)	0.0570	
	1.186	
Total S in coal	1.156	Average.....
	1.167	1.1697
S in Pyrite	0.7470	
S in CaSO ₄ = S as (FeSO ₄ +CaSO ₄) — S as FeSO ₄		
= 0.0570—0.0034 = 0.0536 per cent		
0.0536 per cent S = 0.228 per cent Ca SO ₄		
0.0034 per cent S = 0.0160 per cent Fe SO ₄		
Fe SO ₄ = 0.0160 per cent	=	0.0034 per cent S
Ca SO ₄ = 0.228 per cent	=	0.0570 per cent S
FeS ₂ = 1.397 per cent	=	0.7470 per cent S
Total Sulphur determined	0.8074	per cent
Total Sulphur in coal	1.1697	per cent

Sulphur unaccounted for and probably
existing as organically combined S.....0.3623 per cent

Since the coal used contained 0.863 per cent of carbon dioxide which was liberated on the addition of acid, this carbon dioxide must therefore exist in the original coal in the carbonate condition, very probably as the carbonates of calcium and magnesium. 0.864 per cent of CO₂ is equivalent to 1.965 per cent of CaCO₃. The calcium oxide (CaO) as determined in the ash analysis was 1.574 per cent, which is equivalent to 2.807 per cent of CaCO₃.

The difference between these two values, 2.807—1.965 = 0.842 per cent of calcium measured in terms of calcium carbonate, is unaccounted for and probably exists as calcium silicate and calcium sulphate.

The above has all the CO₂ calculated to CaCO₃, but in reality the coal contains 0.120 per cent of magnesium oxide (MgO), which probably exists as the carbonate, so 0.120 per cent MgO is equivalent to 0.251 per cent MgCO₃ or 0.131 per cent CO₂. Deducting this CO₂ from the total CO₂, it would give the CO₂ equivalent to CaCO₃.

0.863 per cent total CO_2

0.131 per cent CO_2 equivalent to MgO and MgCO_3

0.732 per cent CO_2 which is very probably all CaCO_3

0.732 per cent $\text{CO}_2 = 1.665$ per cent CaCO_3

Total CaCO_3 from $\text{CaO} = 2.807$ per cent

Total CaCO_3 from $\text{CO}_2 = 1.665$ per cent

1.142 per cent of CaCO_3 existing
as CaSO_4 and CaSiO_3 .

CaSO_4 as determined = 0.228 per cent equivalent to 0.167
per cent of CaCO_3 .

1.142 per cent—0.167 per cent = 0.975 per cent CaCO_3 ex-
isting as CaSiO_3 .

0.975 per cent CaCO_3 is equivalent to 1.112 per cent CaSiO_3 .

Summing up the above combinations:

$\text{MgCO}_3 \dots 0.251$ per cent

$\text{CaCO}_3 \dots 1.142$ per cent

$\text{CaSO}_4 \dots 0.228$ per cent

$\text{CaSiO}_3 \dots 1.112$ per cent

$\text{FeSO}_4 \dots 0.0160$ per cent

$\text{FeS}_2 \dots 1.397$ per cent

The remainder of the iron and silica in the ash is probably present as earth or basic iron silicates with some free silica. The ultimate analysis of the ash sums up to 11.387 per cent. The ash, as determined from an average of four determinations, (varying 0.070 per cent from highest to lowest) is 12.030 per cent; the difference of 0.643 per cent is alkali, chlorine, and probably a small amount of combined carbon dioxide, for the ash was determined by blasting to a constant weight in a porcelain crucible and was not carried to complete fusion in platinum.¹

From the data presented, it may be seen that the oxidation of pyrite in fresh lump coal is very slight, and that the sulphur obtained as water-soluble sulphur consists of the mixed sulphates of iron and calcium. The meaning of the term water-soluble sulphur is, therefore, necessarily vague, unless the conditions of its determination are clearly kept in mind. The solubility of calcium sulphate is great enough to cause discrepancies in the results and lead to fallacies in conclusions, unless care is taken to have conditions of determination, such as volume of water used for leaching and length and temperature of digestion always the same. Then it can be assumed, with reasonable safety, that the water-soluble sulphur determinations will all contain equal

¹ Bulletin No. 37, U. of I. Eng. Exp. Sta., Parr and Wheeler, August, 1909.

amounts of calcium sulphate. For the determination of ferrous sulphate, the determination of water-soluble iron would be the best, if the leaching is done quickly with well-boiled distilled water. The practice of digesting the coal with water for any length of time should be discouraged, for oxidation will surely set in, giving, of course, an error.

ADDITIONAL EXPERIMENTS ON MIXED SIZES OF COAL

Series 7, 8 and 9.—Having studied the effect of different pyrite contents on various sizes of coal under different conditions of moisture and temperature, it was decided to study the influence of these variables on a mixture of these sizes. For this purpose the coal was used directly as it came from the crusher; Series 7, 8 and 9 contained 1.4 per cent, 3 per cent and 5 per cent, respectively, of pyrite. The resulting rise in temperature of the wet and dry samples is shown in Fig. 11, 12 and 13. Fig. 14 is a comparative study of the three dry samples of each series, and Fig. 15 shows a similar study of the wet samples.

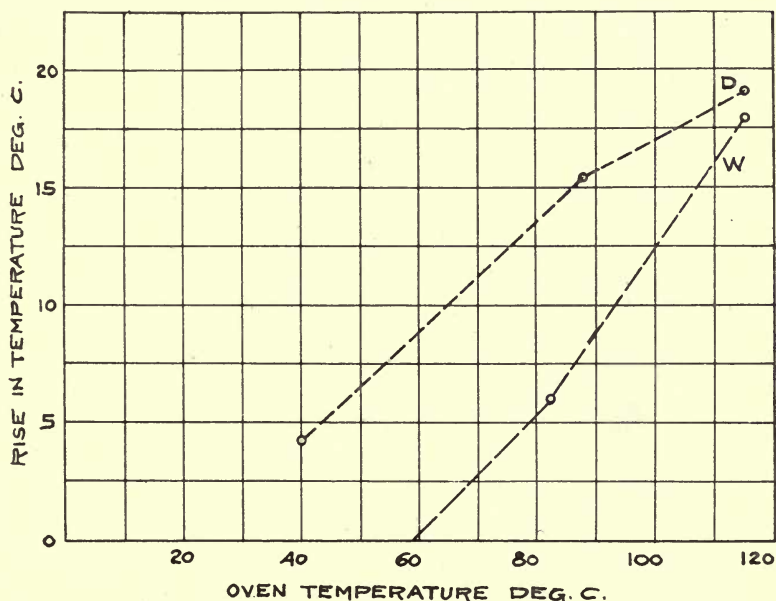


FIG. 11.

SERIES 7—1.4% PYRITE—DRY AND WET COAL.

On account of the increased amount of the larger sizes of coal in these series, the rise in temperature of the coal over the oven temperature did not approach that of some of the fine sizes of the

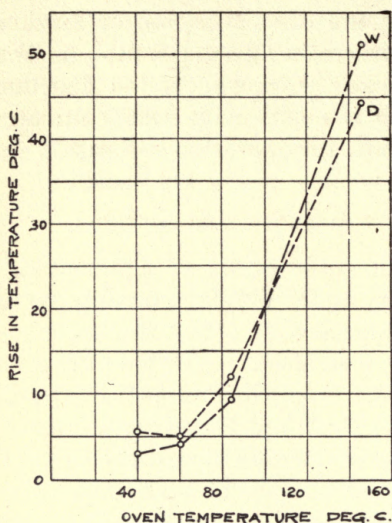


FIG. 12.
SERIES 8—3% PYRITE—DRY AND
WET COAL.

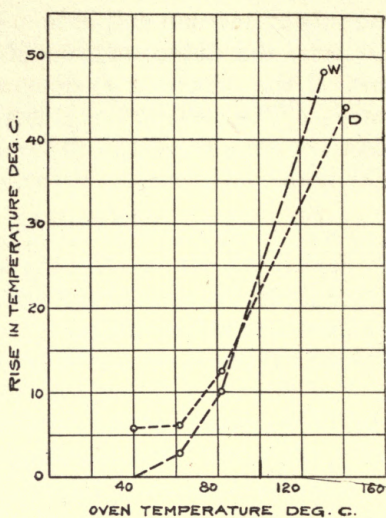


FIG. 13.
SERIES 9—5% PYRITE—DRY AND
WET COAL.

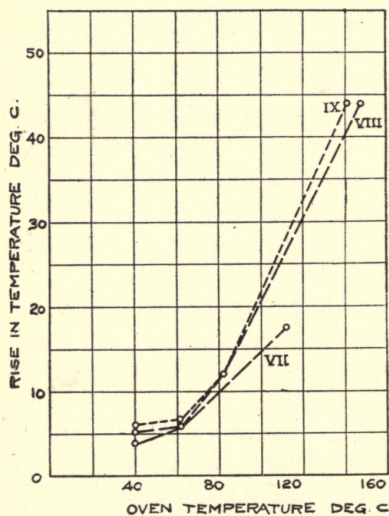


FIG. 14.
SERIES 7, 8, 9—1.4%—3%—5%
PYRITE—DRY COAL.

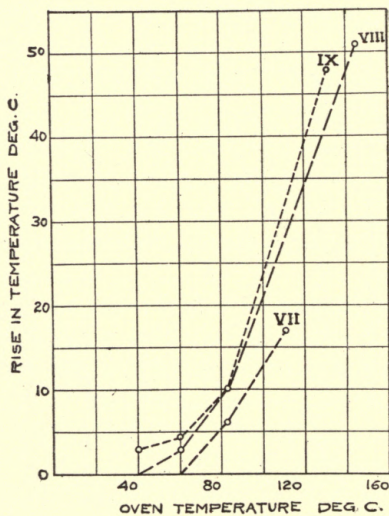


FIG. 15.
SERIES 7, 8, 9—1.4%—3%—5%
PYRITE—WET COAL.

preceding series, but it is seen how much greater the rise in temperature of Series 8 and 9, with their greater pyritic content is over that of Series 7. This is corroborative of the facts disclosed and discussed in the preceding series, and needs no further comment, for Fig. 11 to 15 showing the results are self-explanatory. It may be argued that Series 8 and 9 showed such a marked rise over Series 7 because the oven temperature of the last oven was about 10° higher in Series 8 and 9 than it was in Series 7. This was because of a rather serious accident in the storage battery room which was of such a nature that it could not be remedied without interruption, and so spoiled Series 8 and 9; hence an attempt was made to maintain practically the same temperature as before by reducing the number of heating lights. It hardly seems reasonable, and it might be said, it is almost impossible, that an increase in oven temperature of 10° should cause an increase of the rise in temperature of about 30° , so the only variable left that could cause such a rise is the difference in pyritic content. Why this difference in behavior of these three series, which were identical in composition, size and method of treatment, should be so marked has been shown above; and all that needs to be added is that these series substantiate the results of those preceding.

A STUDY OF POSSIBLE DETERRENTS

Series 10.—Since the relative importance and the influence of the different variables under various conditions seem to have

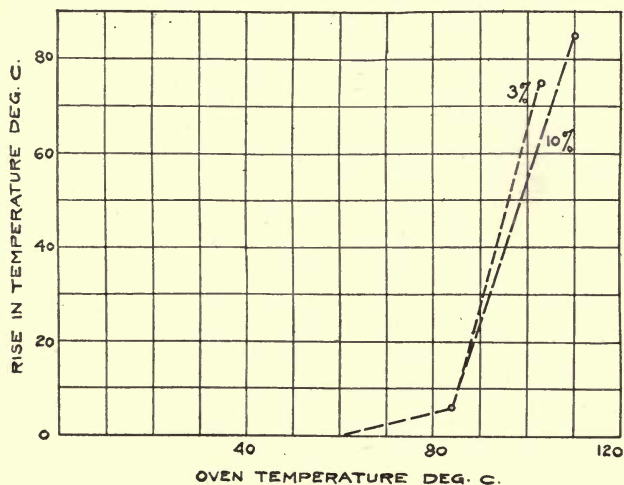


FIG. 16.

SERIES 10—5% PYRITE—SIZE $0\frac{1}{2}$ —3%, 10% NaCl SOLUTION.

been fairly well established, it is natural that an attempt should be made to remove, if possible, this property of self ignition from a mixture of coal that had been known to take fire. As has been explained before, size $0-\frac{1}{8}$, containing 5 per cent pyrite, was decided upon. This size of coal was thoroughly wet with different strengths of various solutions. The 3 per cent solution contained 30 grams of the salt per liter, and the 10 per cent solution contained 100 grams of the salt per liter.

The coal in Series 10 was wet with a solution of sodium chloride so as to study the effect of an inert salt, that is, inert so far as undergoing any reaction with the coal is concerned. This would, therefore, be practically the same as increasing the ash content. Fig. 16 shows that this addition of common salt exerted no retarding influence on the oxidation of the coal, the rise in temperature of the series being about 70° .

Series 11.—A solution of calcium chloride was then used. This salt is very hygroscopic and absorbs moisture with avidity and also retains it, so that it is difficult to dry anything saturated with it. The 3 per cent solution showed no retarding influence, whereas the action of the 10 per cent solution was very marked (see Fig. 17). In the latter case, a rise in temperature of only 26° took place, which shows that a solution of this strength retarded the oxidation very materially. This presumably was not because of any action inhibiting oxidation itself, but merely because so much heat was used in driving off the water.

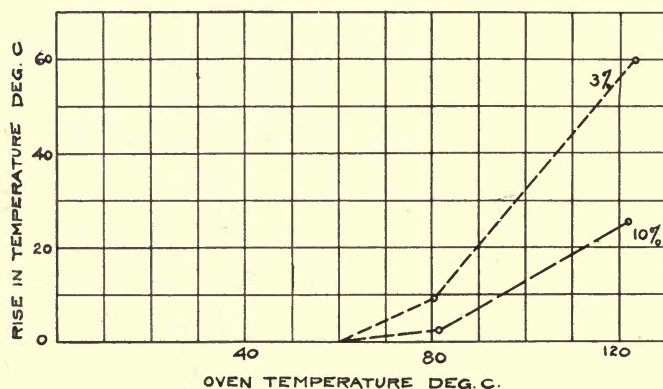


FIG. 17.

SERIES 11—5% PYRITE—SIZE $0-\frac{1}{8}$ —3%, 10% CaCl_2 SOLUTION.

Series 12.—Fig. 18, Series 12 shows the action of a basic substance, for in this series a saturated solution of lime water was used. The rise in temperature was not retarded to any great extent. Lime water was used to see if it would not reduce the oxidation of the pyrite, because in the weathering of the latter substance, a considerable amount of free sulphuric acid is formed. The acid would then combine with the calcium hydroxide to form calcium sulphate. A film of calcium sulphate would then cover every particle of pyrite and thus prevent further oxidation. It was hoped that this action would take place and so keep the temperature down, but the rise in temperature was greater than it was thought it would be, probably because of the heat liberated by the neutralization of the base by the acid.

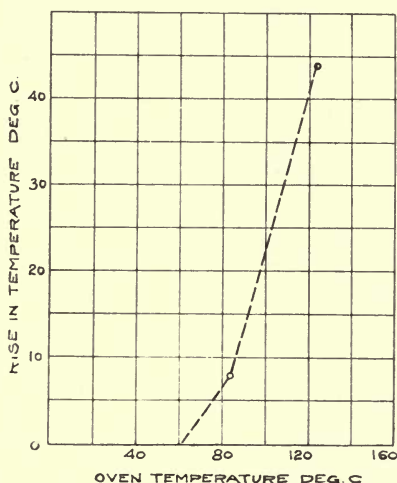


FIG. 18.

SERIES 12—5% PYRITE—SIZE $0\frac{1}{8}$ — $\text{Ca}(\text{OH})_2$ SOLUTION.

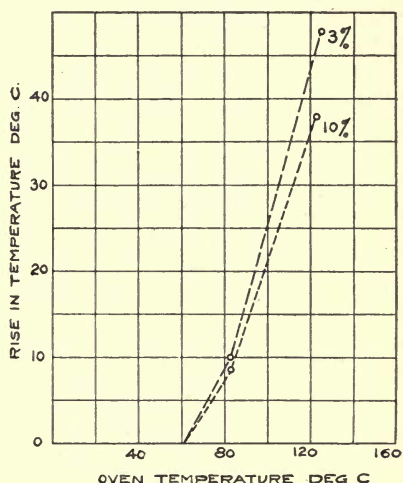


FIG. 19.

SERIES 13—5% PYRITE—SIZE $0\frac{1}{8}$ —3%, 10%, NaHCO_3 SOLUTION.

Series 13.—Since even a solution of sodium bicarbonate, when boiled, gives off carbon dioxide, the effect of its decomposition under a higher temperature was next studied. Also, the sodium carbonate formed would make the coal alkaline and so remove any free acid formed. As seen in Fig. 19, the 10 per cent solution has quite a retarding influence, due in all probability to the absorption of carbon dioxide by the coal instead of oxygen, and so the oxidation is lessened. It is very probable that after some

time the coal would be oxidized to the same degree that it would be if the NaHCO_3 and CO_2 were not present, but the presence of a large amount of carbon dioxide decreases the speed of oxidation, extends the oxidation process over a longer period and so keeps the temperature down to a safe degree.

Series 14.—Ferrous sulphate oxidizes readily and quickly to ferric sulphate and basic ferric sulphate. It was thought that if a considerable amount of ferrous sulphate were added to the coal, it would be oxidized before the coal and retard the oxidation of the latter. This was probably the case, but the heat liberated by the oxidation of the ferrous sulphate just about neutralized its retarding influence, so that the final effect was nearly the same as if the coal had been wet with pure water instead of the ferrous sulphate solution. As seen in Fig. 20, the coal wet with a 10 per

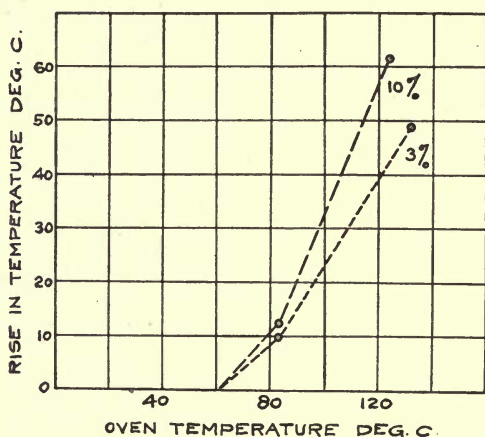


FIG. 20.

SERIES 14—5% PYRITE—SIZE $0-\frac{1}{8}$ —3%, 10% FeSO_4 SOLUTION.

cent solution gave a greater rise than that wet with a 3 per cent solution, the difference in rise of temperature probably being due to the heat liberated by the oxidation of the excess of 7 per cent of ferrous sulphate.

From the above work, it may be seen that the 10 per cent solutions of calcium chloride and sodium bicarbonate retard the oxidation of the coal considerably, although whether or not a

commercial application of the facts disclosed in this work on small amounts of coal is practicable or not is still to be learned from work on large storage units. Since both of these chemicals are fairly cheap, the idea seems reasonable and warrants further investigation.

Series 15.—In this series an attempt was made to determine the effect of intermittent heating and cooling, on the theory that the result of the preliminary heating would bring about those oxidation processes, which, by their cumulative effect, push the temperature up to the danger point, but, when once effected, might not be operative a second time. Three samples were thus tried out: one, (A) of mixed sizes, the same as in Series 10 to 13, with the normal amount (1.45 per cent) of pyrite present; another, (B) designated as 0- $\frac{1}{8}$ size; and the third, (C) a very fine coal dust, obtained by grinding to an impalpable powder in a ball mill. The temperature maintained by the last oven for the first or preliminary heating was 135° to 140°, with a view to carrying the oxidation along to a considerable extent, yet well short of the point of ignition. After cooling and bringing the mass up to the same temperature for the second heating, a more severe test would result than if a lower oven temperature were used. This plan was followed with all but the first sample, which had a preliminary oven-temperature of 120°. The subsequent heating, however, was carried to 140°.

The results of these tests are given in Table 17, page 22. Briefly reviewed, the results are as follows: In the first heating of the oven containing the mixed sizes, (sample A), to 120°, the coal temperature rose 43° above the oven temperature; in the second heating, the coal temperature increased only 11° above the oven temperature, even though the oven temperature was 15° higher in the second heating than in the first. Had the first heating also been up to 135°, the rise in coal temperature would have been greater than 43°, and the difference in the rise of the coal temperature over oven temperature of the two heats would also have been greater. However, the marked retarding effect of pre-heating is well shown in this test.

In the size 0- $\frac{1}{8}$ coal, (sample B), the difference in temperature increase between the first and second heating is much greater, due to the finer size of coal used and also because the oven temperature in both heats was practically the same, the increase

for the first heating being 70° and for the second heating only 19° or a difference in the rise in temperature amounting to 51° .

The very fine coal dust from the ball mill, (sample C), rose to 205° within 48 hours after having been put into the 60° oven. Since the ventilation of the oven was insufficient to carry off the heat as quickly as it was generated, it was impossible to keep the oven temperature down to 60° , the thermometer standing at 69° . The fact that the coal, however, maintained this oven temperature of itself even though a great amount of heat was being continually lost because of the ventilating system, shows how large an amount of oxidation took place. After cooling for 3 days and then reheating at 60° , the coal temperature rose to 73° in an oven temperature of 64° , causing only a 9° rise, whereas in the first heating at this temperature a 136° rise took place. The coal was then placed in the high temperature oven, and this oven was then heated up to 147° for three days. At the end of this time, the coal temperature was 220° , a rise of only 73° over the oven temperature. If this coal had been put into this oven first, without preheating, it would undoubtedly have taken fire at once, i. e., in 24 or 36 hours. However, as it was, the coal did not take fire until it was removed from the oven and exposed to the air. The fact that the coal did take fire after removing it from the oven shows that the time of oxidation (3 days) in the oven was not great enough to allow a thorough oxidation, although the behavior of the coal in the first two heats at 60° is of immense value in showing the effect of preheating. This particular sample of coal, ground as fine as it was, represents of course an exaggerated condition, not likely to be found under practical conditions of storage, but it was used to illustrate clearly the effect of preheating, which was shown so strikingly when the coal first indicated a rise in temperature of 136° at 69° oven temperature and then showed a rise of only 9° the second time it was heated to that temperature. It should be noted also that in the third heating, the oven temperature was sufficiently high to produce that type of oxidation which results in the formation of CO_2 . This, with the marked property of condensation or occlusion of oxygen by the very finely-divided material, would be expected to result in a marked increase of temperature, quite distinct from what would occur with an oven temperature of only 60° .

To show the results on these three samples in a diagrammatic

form, an attempt is made in Fig. 21, wherein the heat area is divided in the center. Points representing the increase of temperature in the first or preliminary heating are located in the left-hand area and the points representing the increase of temperature during the second heating are located in the right-hand area. In order, then to show the relation as to differences of increase, the points for the same coal in the two areas are connected by a straight line.

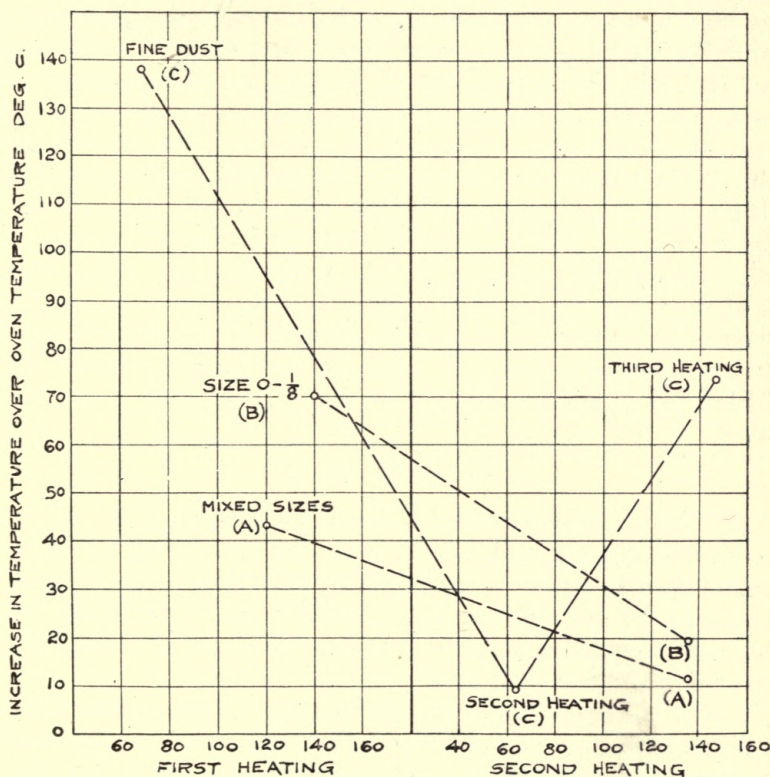


FIG. 21.
SERIES 15.

ADDITIONAL DATA

Railway Storage of Coal.—On account of the general strike of bituminous coal miners in the early spring of 1910, many of the large users of coal, such as the railroads, stored large quantities of coal for future use. In reply to a circular letter sent out for

the purpose of gathering data and information concerning this coal in actual storage, Mr. P. Maher, Superintendent of Motive Power of the Chicago and Alton Railroad Company, reports as follows. A pile containing 2250 tons, 6 ft. high, 300 ft. long and 8 ft. wide, of run-of-mine, Springfield district coal, stored at Slater, Illinois, 1½ months after storage, showed 30 per cent slack, and the company was not getting results from the storage coal such as were obtained from similar coal fresh from the mine. A pile of the same kind and size of coal stored at Brighton Park, Illinois, containing 3300 tons, crumbled into 20 per cent of slack. This pile was 6 ft. high, 372 ft. long and 41 ft. wide. A pile of similar coal stored at Ridgely, Illinois, containing 19710 tons, showed 35 per cent of slack and took fire in several places. This pile was 10 ft. high, 330 ft. long and 80 ft. wide. The reason that the latter pile took fire and the former two did not was probably due to the increased height. It is to be noted that the first two piles were 6 ft. high, while the third was 10 ft. Also, the first two piles were 8 and 41 ft. wide, respectively, while the third was 80 ft. wide. Presumably, in the first two cases, the radiation of heat in the initial stages was sufficient to keep the rise in temperature from reaching the point where the more active processes were set in motion.

IV. CONCLUSIONS

1. The oxidation of coal is continuous over a wide range of time and conditions, and begins with the freshly-mined coal at ordinary temperatures. A number of oxidation processes are involved, which are more or less distinct in character, some being relatively slow and moderate in form, while others are rapid and vigorous in their action.

2. In general it may be said that for a given coal a point exists, as indicated by the temperature, below which oxidation is not ultimately destructive. The continuance of this point is dependent upon certain accessory conditions; if these conditions are withdrawn, the oxidation ceases. On the other hand, above this critical point, which is best indicated by temperature, oxidation is ultimately destructive and is characterized by the fact that it does not depend for its continuance upon external conditions, but is self-propelling or autogenous.

3. The point of autogenous oxidation, while varying for dif-

ferent conditions, may be indicated by temperatures of the mass ranging from 140° to 160°C. , in an atmosphere of oxygen, or approximately between 200° to 275°C. in oxygen diluted with nitrogen, as in air, depending to a great extent upon the fineness of division. The phenomenon of fire or actual kindling does not occur until a much higher temperature is reached, usually beyond 350°C.

4. The temperature at which autogenous oxidation begins is the sum of numerous temperature components, each one of which, either because of its own contribution to the total heat quantity or because of its function as a stimulus for chemical activities, must be looked upon as a dangerous factor, tending directly to the ultimate result of active combustion throughout the mass. An enumeration of the more important elements which contribute towards this end are the following:

a. External Sources of Heat.—Oxidation, especially of the lower or moderate form, is greatly accelerated and in certain phases directly dependent upon an increase of temperature. What may be external or physical sources of heat, and thus presumably avoidable, are suggested by the following:

(1) Contact of the mass with steam pipes, hot walls or floors under which are placed heat conduits of any sort.

(2) The heat of impact or pressure due to the method of unloading or to the depth of piling.

(3) Climatic or seasonal temperature at the time of storage.

(4) The direct absorption of heat from the sun or from reflecting surfaces.

b. Fineness of Division.—Coal in a fine state of division presents a very much larger surface and brings a much larger quantity of reacting substances in contact with oxygen than when in solid masses. Under these conditions, with a condensation or accumulation of relatively large amounts of oxygen immediately surrounding or in contact with the particles of carbonaceous matter, the circumstances are exceedingly favorable for rapid oxidation upon the arrival of the mass to a suitable temperature. But more especially does this fineness of division facilitate the initial form of oxidation described under *c* below.

c. Easily Oxidizable Compounds.—A first or initial stage of oxidation exists in bituminous coals which does not result in the

formation of CO_2 . There are present in coals of this type, unsaturated compounds, which have a marked avidity for oxygen at ordinary temperatures, the products being humic acid or other fixed constituents of the coal texture. Coals vary widely in this respect, and it has been proposed by some to regard this property as an index of the liability to spontaneous combustion. It is, however, very largely dependent upon the freshness of the coal and upon the fineness of division, (see *b* above,) and should be looked upon as a contributing factor, though in coals of the Illinois type, at least, with their high per cent of sulphur, this action should doubtless be considered second in importance to that of iron pyrites.

d. Iron Pyrites.—The presence of sulphur in the form of iron pyrites is a positive source of heat due to the reaction between sulphur and oxygen. This may be conveniently referred to as the second stage in the process of oxidation. Here again rapidity of oxidation is directly dependent upon fineness of division. Since coals, as a rule, have a much higher earthy or ash content in the fine duff, and since iron pyrites is a large component of this material, it follows that the presence of dust or duff in all coals of the Illinois type is a positive source of danger. Since coals of the Illinois or mid-continental field have in the larger number of cases iron pyrites averaging over 6 per cent, or, as sulphur above 3 per cent, the heat increment from the oxidation of only $\frac{1}{3}$ of this material is sufficient to raise the temperature of the mass approximately 70° , assuming that there is no loss by radiation. Under usual conditions, and especially considering the greatly accelerated rate of chemical activity accompanying a rise of temperature, this oxidation may proceed with such rapidity that the heating up of the mass will be but little affected by loss of heat due to radiation, except in relatively shallow piles.

e. Moisture. Moisture, while essential to pyritic oxidation, is given separate mention because its importance is apt to be underestimated. Any coal with conditions favorable to oxidation will be facilitated in that action by moisture. It is to be noted in this connection that the normal water content or vein moisture of coals in this region is rarely below 10 per cent and ranges usually from 12 per cent to 15 per cent. The presence of such water must be borne in mind in considering the likelihood of chemical activity on the part of the pyrites present. Without exception, in all the series of tests, *the wetting of the coal increased the activity as shown by the ultimate temperature.*

f. The Oxidation of Carbon and Hydrogen. A third stage of oxidation of the carbonaceous material exists by reason of the tendency of certain of the hydrocarbon compounds of coal to oxidize with the formation of CO_2 and H_2O at temperatures in excess of 120° to 140° . Though this type of oxidation does not take place appreciably at ordinary temperatures, it must be looked upon as an exceedingly dangerous stage in the process of oxidation, owing to the very much higher quantity of heat which is discharged by the oxidation of carbon and hydrogen; so that the temperature of autogenous action, though ordinarily occurring at a higher point by 100° or more, may be quickly attained as a result of this form of oxidation. Any initial heat increments, therefore, which threaten to bring the chemical activities along to the point where the oxidation processes invade the carbonaceous material in this manner must be looked upon as dangerous. For example, any of the initial or contributory processes which result in raising the temperature of the mass 50° above the ordinary temperature, would, in all probability, have enough material of the sort involved in such action to continue the activity until another 50° had been added, which would thereby attain to the condition wherein this third type of oxidation would begin.

g. The fourth stage of oxidation may be indicated as occurring at temperatures above 200° to 275° and differs from the previous stages in that the action is autogenous and not dependent upon other sources of heat to keep up the reacting temperature. Activity in this stage is further accelerated by the fact that above 300° the decomposition of the coal begins, which is exothermic in character, thereby contributing somewhat to a further increase in temperature. The ignition temperature is reached at a point still further along, usually in excess of 300° to 400°C .

5. The above formulation of the various stages and types of oxidation clearly indicates the principles which must be observed in any attempt at the prevention of spontaneous combustion. The following enumeration, therefore, of preventative or precautionary measures is to be considered as suggestive rather than complete in character.

a. The avoidance of an external source of heat which may in any way contribute toward increasing the temperature of the mass is a first and prime essential.

b. There must be an elimination of coal dust or finely-divided material. This will reduce to a minimum the initial oxidation processes of both the carbonaceous matter and the iron pyrites. These lower forms of oxidation are to be looked upon as forces, without which it would be impossible for the more active and destructive activities to become operative.

c. Dryness in storage and a continuation of the dry state, together with an absence of finely-divided material, would practically eliminate the oxidation of the iron pyrites.

d. Artificial treatment with specific chemicals or solutions intended to act as deterrents does not offer great encouragement, though some results seem to warrant further trial in this direction.

e. By means of a preliminary heating, the low or initial stages of oxidation are effected. These sources of contributory heat being removed, the forms of destructive oxidation are without the essential of a high starting temperature and are therefore inoperative. Whether such preliminary treatment is within the realm of practical or industrial possibility could not, of course, be determined within the scope of these experiments.

f. The submerging of coal, it is very evident, will eliminate all of the elements which contribute toward the initial temperatures. As to its industrial practicability, like the conditions under *e* above, it can best be determined by actual experience.

g. Other processes may be suggested by the formulation of the principles involved. Such, for example, would be the distribution throughout the coal of cooling pipes through which a liquid would circulate having a lower temperature than the mass. This would serve to carry away any accumulation of heat and confine the oxidation to the lower stages only. On the contrary the proposition sometimes made to provide circulating passages for the transmission of air currents is of questionable value, since it may result in the contribution of more heat by the added accessibility of oxygen than will be carried away by the movement of the air.

APPENDIX



APPENDIX

HISTORICAL REVIEW WITH SUMMARY OF OPINIONS

The literature upon the spontaneous combustion of coal is widely scattered and difficult of access to a majority of those most directly interested in the topic. In this series of investigations, a considerable amount of time has been spent in assembling these discussions and making synopses of the same. In order that the results of this phase of the work may be made accessible, a review of the literature upon spontaneous combustion is presented in this Appendix.

Grundmann's¹ work, published in 1862, was probably the first serious attempt to study the weathering losses of coal. He found that while the coals lost gaseous constituents, they gained in hygroscopic moisture and so the specific gravity of the coal remained constant. He states that large pieces weather less than fine coal, and that rain and increased temperature accelerate the weathering. Using the percentage of ash as a basis to calculate the change in weight that took place during storage, he found that a pile of 300 tons lost 58 per cent in weight in nine months.

Reder² in 1866 was among the first to follow up Grundmann's work. He found that storing coal for a year caused a deterioration in the heating value; but, contrary to Grundmann's results, he found no appreciable loss in weight.

In 1865, Varrentrapp³ reviewed Grundmann's work of 1862. Varrentrapp and other later workers could not duplicate the results of Grundmann, and ascribe his errors to poor sampling. Varrentrapp found from his experiments in storing coal that the oxidation of fresh coal is very rapid, and within the heap leads to a rise in temperature, which, however, is very far from the ignition point.

He states, however, that temperatures reaching the ignition point and causing combustion have at times been found.

¹ Carnall Zeitschrift, Vol. X, page 236, 1862.

Zeitschrift für Berg, Hutten, und Salienwesen im preussischen Staate, Band IX und X.

² Oesterr. Zeitschrift für Berg und Hutten, Vol. XV, 1867.

³ Dingler's Polytechnic Journal, 1865, Vol. 175, page 168. Vol. 178, page 379.

L. Thompson¹ in 1865 found that dry coal in storage for six months lost $\frac{1}{3}$ of its calorific value; if, however, the coal was moist, the loss was much greater. He divides the weathering of bituminous coals into two classes known as "dry rot" and "wet rot". The latter he considers to be a sort of fermentation in which a part of the hydrogen escapes and some of the carbon is oxidized to carbon dioxide; in this way the coal loses calorific value in two directions.

Fleck² in 1865 examined a series of six Saxon coals which had been preserved in a cabinet since 1856. The results of his examination were compared with analyses made nine years previously, when, it is presumed, the coals were in a fresh state. After such an exposure in a dry place, three of the number, it was inferred, showed an important increase in proportion of ashes together with a corresponding decrease of organic matter, while the ashes of the remaining three appeared to have decreased. The explanation of such unlike results was sought by Fleck in the lack of uniformity of the related samples, especially as to the ratio of ashes. An increase of oxygen and of indisposable hydrogen was observed in each case, together with a loss of carbon and of disposable hydrogen. Hence the conclusion that, at ordinary temperatures, bituminous coal sustains a loss in carbon and of disposable hydrogen, and proportionately a loss in calorific value, which is increased in proportion to the addition of combined water.

The most careful of the early experiments made on this subject were those of Dr. Richter³ from 1868 to 1870. He concluded that the weathering of coal was due to the absorption of oxygen, part of which goes to the oxidation of carbon and of hydrogen in the coal, and part of which is taken into the composition of the coal itself; that if the heap becomes warm, either through this process or through any other cause, the action is accelerated, but then falls off, and becomes so slow that the changes effected within a year

¹ London Journal of Arts, June, 1865, page 321.

Dingler's Poly. Journal, 1865, Vol. 178, page 161.

² Technik der Steinkolen Deutschlands. 1865, Vol. II, page 221.

Transactions of the American Institute of Mining Engineers, Vol. 8, page 207.

³ The Gas World. April 13, 1901.

Dingler's Poly. Journal, Vol. 190, page 398; Vol. 195, page 315; Vol. 195, page 449.
Vol. 193, page 54; Vol. 193, page 264.

become difficult to estimate; that moisture, as such, has no direct influence upon the process apart from the presence of pyrites or from the coal crumbling down more rapidly when wet than when dry and, therefore, more rapidly heating up; that if the temperature does not go beyond certain limits (338° to 374° F.) there is no appreciable loss of weight, but rather, on the whole, a gain through the absorption of oxygen. Also, that it is not necessary to explain the loss in heating value, of coking power, and of gas yield by any theory of new arrangements of atoms, for it is sufficient to look at the absolute loss of carbon and hydrogen and the increase in the proportion of oxygen. At a later date, he concluded that large coal was affected less than small, not because it had less surface, but because small coal was a more active absorbent of oxygen, and, therefore, became more rapidly heated; that air-ways in a heap would have to be very numerous in order to prevent any rise in temperature; and that the heap ought to be so constructed as not to allow air to get from the air-ways into the bulk of the coal.

Haedicke¹ in 1880 assigned to pyrites the leading part in spontaneous ignition, conditioned on allowing the temperature to rise sufficiently.

Professor Fischer² of Gottingen, in his work on this subject prior to 1901 concluded that storage depreciation and spontaneous ignition were phenomena of oxidation; the part which is played by iron sulphide was disputed, but the variances which have given rise to the uncertainty were due to the differences between the different sulphides of iron present in coal. He claims that marcasite, for example, is much more weatherable than ordinary pyrite. Actual wetting is much more promotive of oxidation of the iron sulphide than heating in dry or even moist air. Besides this, Fischer finds that many coals contain sulphur in the form of unsaturated organic compounds. He finds that those coals which rapidly absorb bromine are those which are most liable to rapid oxidation and spontaneous ignition; as a practical test, he recommends shaking a gram of the finely powdered coal with 20 c. c. of a half-normal solution of bromine for five minutes. Then, if the smell of bromine has not disappeared the coal may safely be put in storage; if it has, the coal should be used up as soon as

¹ The Gas World, April 13, 1901.

² *ibid.*

possible. The absorption of oxygen by the unsaturated organic compounds referred to is accompanied by a gain in weight and at the same time by a rise in temperature; and the warmer the mass the more rapidly does the oxidation go on, so that the temperature is apt to rise to a dangerous extent. Concurrently with the oxidation of these products, is the oxidation of another set of organic compounds with evolution of carbon dioxide and water vapor, and this results, not in a gain, but in a loss of weight. Whether the mass as a whole gains or loses weight is, therefore, a question of the composition of the coal, but the loss in weight is in no case great. Covering wet slack coal with other coal is apt to produce spontaneous ignition; the danger here appears to arise from the sulphide of iron rather than from the organic compounds. Fischer regards ventilation of the coal heap with suspicion, not because the idea is in itself a wrong one, but because it is not practicable to ventilate the whole heap efficiently. He claims that the coal should be stored dry and kept dry under cover, and in layers not too deep.

In a paper read before the German Gas Association in 1900, Herr Sohren,¹ Manager at Bonn, stated that it is no longer possible for many reasons to work gasworks with a supply of coal renewed from month to month; and that all questions affecting storage have, therefore, a continually increasing importance. Undoubtedly there is a greater or less depreciation in the quality of coal kept in store, and the causes of this have attracted a good deal of attention; though, on the whole, it is surprising to find to how great an extent the study of the chemistry of coal has been neglected. Questions of this nature assumed importance in connection with the spontaneous ignition of cargoes of coal in ships; in 1874, out of a list of 4485 coal laden ships, no fewer than 60 caught fire.

In a paper read by Professor Vivian B. Lewes² at the 31st Session of the Institution of Naval Architects held at the Society of Arts, Adelphi, the author began by referring to the appointment of a Royal Commission in 1875 on the proposition of the Board of Trade and a Committee of Lloyds, to investigate the causes of the spontaneous ignition of coal cargoes, which had en-

¹ The Gas World, April 13, 1901.

² The Journal of Gas Lighting, Vol. 55, page 645.

The Journal of the Society of Chemical Industry, Vol. 9, page 483.

tailed serious loss of life and destruction of property. The Commission was assisted by Dr. Percy and Sir Fred Abel.

From 1875 to 1883 no less than 57 coal laden vessels were known to have been lost, while during the same period 328 were missing from unknown causes, though probably a large proportion of these losses were due to spontaneous combustion. In view of this fact, it was suggested to the author that an inquiry into the causes and possible prevention of this serious evil was greatly needed in the Royal Navy as well as in the merchant service; he therefore undertook it, and laid the results before the members of the Institute.

The author proceeded to point out that, besides the carbon hydrocarbons, coal contains certain mineral substances, as sulphate of lime or gypsum, silica, and alumina, while in nearly all kinds there is to be found disulphide of iron, "brasses" or pyrites. Of these constituents, those that are likely to produce heat and cause spontaneous ignition in newly-won coal are the carbon, hydrocarbons, and brasses, which, when they come in contact with air and moisture, give rise to certain chemical actions. He then described at length the influence of each of these substances in the production of heat. Taking carbon first, he remarked that it is one of those substances which possess to an extraordinary degree the power of attracting and condensing gases upon their surfaces, the power varying with the state of division and density of the particular form of carbon used. In the case of newly-won coals, the least absorptive would, he said, take up one and one-fourth times, and others would absorb three times, their own volume of oxygen. This absorption is very rapid at first, but gradually decreases, and is influenced to a very great extent by temperature. Air-dried coal absorbs oxygen more quickly than wet coal.

Dealing in the next place with the action of the bituminous constituents of coal in causing spontaneous ignition, the author explained that all coal contains a certain percentage of hydrogen, which is in combination with some of the carbon and also with the nitrogen and oxygen, and forms with them the volatile matter in the coal. The amount present in this condition varies very largely, being very small in anthracite and very great in cannel and shale. When the carbon of the coal absorbs oxygen, the compressed gas becomes chemically active and soon commences

to combine with the carbon and hydrogen of the bituminous portions, converting them into carbon dioxide and water. This chemical activity increases rapidly with rise of temperature, so that the heat generated by the absorption of the oxygen causes the latter to enter rapidly into chemical combination. Chemical combination of this kind, i. e., oxidation, is always accompanied by evolution of heat; and this further rise of temperature again increases the rapidity of oxidation, so that a steady rise of temperature is set up. This taking place in the center of a heap of small coal, which from the air and other gases enclosed in its interstices is an admirable non-conductor of heat, will often cause such heating of the mass that, if air can percolate slowly into the heap in sufficient quantity to supply the necessary percentage of oxygen for the continuance of the action, the ignition point of the coal would soon be reached. It has been suggested that very bituminous coal (such as cannel, shale, and coals containing schist) is liable to spontaneous ignition from the fact that a rise in temperature would cause heavy oils to exude from them, and by undergoing oxidation, might cause rapid heating. Experiment, however, not only shows that this is not the case, but that the heavy mineral oils have a remarkable influence in retarding heating.

The action of iron disulphide, pyrites, or "brasses," in promoting spontaneous ignition was next discussed. The author said that ever since Berzelius first expressed the opinion that the heat given out by the oxidation of iron disulphide into sulphates of iron might have an important bearing on the heating and ignition of coal, it had been adopted as the popular explanation of that phenomenon; and, although the work of Richter clearly proved that this is not the case, the old explanation was still given. Dr. Percy in 1864 pointed out that oxidation of the coal also probably had something to do with spontaneous combustion, a prediction amply verified by Richter's researches some six years later. This disulphide of iron was found in coal in several different forms, sometimes as a dark powder distributed throughout the mass of the coal, and scarcely to be distinguished from coal itself. In larger quantities, it often occurred as thin golden-looking layers in the cleavage of the coal, while it sometimes occurred as large masses and veins, often from 1 in. to 2 in. in thickness; but inasmuch as these masses of pyrites were very heavy, they

rarely found their way into the screened coal for shipment, many hundreds of tons of these brasses being annually picked out from the coal at the pit's mouth and utilized in various manufacturing processes. When the air was dry, the pyrites underwent but little change at ordinary temperatures. In moist air, however, they rapidly oxidized when in a finely-divided condition, the first action being the formation of ferrous sulphate and sulphur dioxide, together with the liberation of sulphur. The relative amounts of the latter were regulated by the temperature and the supply of air, while longer contact with moist air converted the ferrous sulphate into a basic ferric sulphate generally termed "misy". It was during this process of oxidation that the heat supposed to cause the ignition was evolved. But when it was considered that some of the coals most prone to spontaneous combustion contained only 0.8 per cent of iron pyrites, and rarely more than 1.25 per cent, the absurdity of imagining this to be the only cause of ignition became manifest. If 100 pounds of coal were taken, and the whole of the pyrites in it concentrated in one spot and rapidly oxidized to sulphate, the temperature would barely be raised to 100°C . if all loss of heat could be avoided. The author had carefully determined the ignition points of various kinds of coal, and found them to be as follows:—

Cannel.....	698°F. = 370°C.
Hartlepool.....	766°F. = 408°C.
Lignite.....	842°F. = 450°C.
Welsh steam.....	870½°F. = 477°C.

Hence, no stretch of imagination could endow the small trace of pyrites scattered through a large mass of coal, and undergoing slow oxidation, with the power of reaching the needful temperature. Richter fully realized this point, and discarded the idea of the pyrites doing anything more than adding its mite to the causes which bring about rise of temperature. In this, however, Lewes thought Richter was mistaken, his own experiments pointing to the fact that they might increase the liability to ignition when present in large quantities, and that they do so by liberating sulphur under certain conditions. A still more important part played by the pyrites, is that as it becomes oxidized to ferrous sulphate it swells in size and so tends to split up the coal into small pieces, and, by exposing a large extent of fresh surface to the air, causes increase of temperature and energetic chemical action.

The author, Lewes, then traced the actions which culminate in ignition. He said that on newly-won coal being brought to the mouth of the pit, it at once began, by virtue of its surface action, to absorb oxygen from the air. Unless piled in unusually large heaps and a good deal broken, it did not, however, as a rule, show signs of heating, as the exposed surface was comparatively small; and the air finding its way freely between the lumps kept down the temperature. The coal was now screened, and the obtrusively large lumps of brasses picked out. It was then put into trucks, and enjoyed the disintegrating processes of joltings and shuntings innumerable, every jar adding to the percentage of small coal present, and causing a corresponding increase in the size of the surface exposed to the air. Arrived at the docks, it had to be transferred from the truck to the ship, which was done by one of the numerous forms of tips, shoots, or spouts employed for the purpose; and it was during this operation that more harm was done than at any other period. The coal first shot into the vessel was, by reason of the distance which it had to fall, broken down into small lumps, and, having to bear the impact of the succeeding load falling upon it from a height, rapidly became powdered into slack; while the succeeding loads, falling in on the cone so formed, became more or less broken down so that by the time the cargo was all taken in, a dense mass of small coal was to be found under the hatchway. It was invariably at this point that heating took place, as the large surface exposed fresh to the air by the breaking down of the coal caused rapid absorption of oxygen, and consequent rise of temperature. This set up chemical combination between the oxygen absorbed by the coal, and the hydrocarbons and coal "brasses". The combination of the "brasses" with oxygen caused the swelling of the oxidized mass and the splitting up of the coal. Fresh surfaces were exposed, and more absorption of oxygen took place, the ignition point of the sulphur vapor and sulphur compounds distilled out of the pyrites was reached, and rapidly raised the temperature to the ignition point of the coal. It was only in cases where large quantities of dense coal brasses were present, however, that this action could occur. On examining the evidence to be obtained as to the conditions under which spontaneous ignition of coal ships usually takes place, Lewes found that the liability to such accidents increases with

- (1) The tonnage of the cargoes,
- (2) The ports to which shipments are made,
- (3) The kind of coal of which the cargo consists,
- (4) The size of the coal,
- (5) The shipping of coal rich in pyrites while wet,
- (6) The ventilation of the cargo,
- (7) The rise in temperature in steam colliers due to the introduction of triple-expansion engines and high pressure boilers.

Having discussed the chemical and physical conditions which lead to the spontaneous ignition of coal, the author proceeded to formulate precautions tending to prevent such disasters. These had reference to the choice of coal for shipment to distant ports, and to the precautions to be taken during shipment and when the coal is on board. He advised that the coal should be as large as possible, free from dust, and have as little "smalls" as practicable. It should be as free from pyrites as possible, in order to prevent disintegration after shipment; and it should contain when air-dried not more than three per cent of moisture. No coal should, he said, be shipped to distant ports until at least a month had elapsed after it was brought to the surface of the pit's mouth. Every precaution should be taken to prevent the breaking up of the coal while being taken on board, and on no account should any accumulation of fine coal be allowed under the hatchways. When possible, the coal should be shipped dry, as external wetness, by producing oxidation of the pyrites, caused disintegration. When the coal had all been taken in, it should be battened down and the hatches not opened again until the vessel reached her destination, the only ventilation allowable being a 2-in. pipe just inserted into the crown of each coal compartment, and led 12 ft. up the nearest mast, the top being left open. This would be quite sufficient to allow free egress to any gases evolved by the coals, but would not allow undue access of air. Into the body of the coal cargo itself would be screwed, at regular intervals of about six feet, iron pipes, closed at the bottom and containing electrical alarm thermometers, set at a certain temperature, the attainment of which would be indicated by the ringing of a bell which would not cease until the temperature had again fallen, and then the spot in which the heating had taken place would be indicated by an index-board. The existence of overheating having been reported by the bell and recorded by the index, the author offered

suggestions for suppressing it. He advocated the injection of compressed carbonic acid gas, and explained his plan as follows: The nozzle attached to the screw valve on the bottle of condensed gas would have a short metal nose-piece screwed on it, the tube of which would be cast in solid, with an alloy of tin, lead, bismuth and cadmium, which could be so made as to melt at exactly 200° F. (93° C). The valve would then be opened, and the steel bottle buried in the coal during the process of loading. The temperature at which the fusible metal plug would melt is well above the temperature which could be reached by any legitimate cause, and would mean that active heating was going on in the coal. Under these conditions the pressure in the steel cylinder would have reached something like 1700 pounds; and the moment the plug melted, the whole contents of the bottle would be blown out of it into the surrounding coal, producing a large zone of intense cold, and cooling the whole of the surrounding mass to a comparatively low temperature. The action, moreover, would not stop here, as the cold, heavy gas would remain for some time in contact with the coal, diffusion taking place but slowly through the small exit-pipe. When coal has absorbed as much oxygen as it can, it still retains the power of taking in a considerable volume of carbonic acid gas; and when coal has heated and then has been rapidly quenched, the amount of gas so absorbed is very large indeed, and the inert gas so taken up remains in the pores of the coal and prevents any further tendency to heating. Indeed, a coal which has once heated, if only to a slight degree, and has then cooled down, is perfectly harmless and will not heat a second time. It is not by any means necessary to replace the whole of the air in the interstices of the coal with the gas, as a long series of experiments shows that 60 per cent of carbonic acid gas prevents the ignition of the pyrophoric substances. One hundred cu. ft. of gas can be condensed in the liquid state in a steel cylinder 1 ft. long and 3 in. in diameter; and it has been shown that a ton of coal contains air spaces equal to about 12 cu. ft. One of these cylinders would therefore have to be put in for every eight tons of coal, and these would be distributed evenly throughout the cargo, and near the alarm thermometers, which would be set to ring a degree or two below the point at which the fusible plug would melt. The bell ringing in the captain's room would warn him that heating was taking place, and the bell would continue to

ring until the cylinder had discharged its contents and had cooled down to a safe degree, so that the whole arrangement would be purely automatic, and yet the officers would know if everything were safe. If the precautions advocated were taken, no danger could arise until the arrival of the ship at her destination, and the commonest precautions would then suffice.

In conclusion, the author remarked that the question of preventing the heating and ignition of stores of coal on land and ready for use in bunkers could not be met so well by the use of the liquid gas; and in these cases it would be found beneficial to dress the coals with a little tar or tar oil, which would close the pores, and to a great extent prevent oxidation. He believed this was advocated by Lachman about 1870. Crude petroleum in small quantities would also be found valuable for this purpose, for it has no tendency to oxidize itself, and lowers the tendency in other bodies, besides coating them and so preventing access of oxygen.

In a later paper, Professor Lewes¹ of the Royal Naval College says that, in the spontaneous ignition of coal stored in bulk, the oxidation of the pyrites present plays only a very subsidiary part, the chief factor being the surface condensation of the oxygen in the pores of the coal and the action of the condensed gas in effecting the oxidation of the hydrocarbons present in the coal. While sufficient ventilation to prevent any considerable increase in temperature within the mass is effective in preventing ignition, it is practically impossible to maintain this condition in large coal stores or in a cargo on board ship, where usually only enough air enters to lead to dangerous heating. The recent suggestion to wet thoroughly the whole mass of coal is impracticable, owing to the great increase in weight brought about if sufficient water is added so as to be effective; too small a quantity of water only accentuates the danger.

A. O. Doane² in 1904 stated that the amount of moisture present in a bituminous fuel after drying in the air is a measure of the risk of spontaneous ignition when the fuel is stored; bituminous coals containing over 4.75 per cent of moisture are dangerous. Coal bins should be of iron or steel, protected by concrete, and should be roofed over. Free air passages should

¹ The Journal of Gas Lighting, 1906, page 33.

The Journal of the Society of Chemical Industry, Vol. 25, page 463.

² Engineering News, Vol. 52, page 141.

The Journal of the Society of Chemical Industry, Vol. 23, page 1203.

be provided around the walls and beneath the bins so as to keep them cool, and the depth of coal stored should not be over 12 ft. The customary method of providing air passages in the body of the fuel is useless, since it tends merely to accelerate oxidation and does not produce a sufficient current of air to keep the temperature down. Cracks or joints in the walls of the fuel bin increase the risk of spontaneous ignition for similar reasons.

Durand¹ has explained the spontaneous ignition of coal as being due to the presence of pyrites, which on oxidation under suitable conditions inflames, and then sets fire to the coal in which it is embedded.

According to Fayol's experiments², however, the real cause of spontaneous combustion is the oxidation of the coal itself and not that of the pyrites. The absorption of oxygen by coal takes place more or less readily, depending upon the initial temperature and upon the coal being more or less finely divided. Lignite in the state of fine dust takes fire at 150°, gas coal at 200°, coke at 250° and anthracite at 300° or above. On heating a mixture of finely powdered coal and pyrites up to 200° for four days, the coal took up 6 per cent of oxygen, while the pyrites absorbed only 3.5 per cent. Hence coal absorbs oxygen much more energetically than pyrite does, a fact which was confirmed by the following experiment. 900 gr. of powdered coal and 3350 gr. of powdered pyrites were placed in tin cans and put in a drying chamber. Up to 135° both behaved similarly, but from there on the temperature of the pyrites remained almost stationary while that of the coal quickly rose, ignition taking place a few hours afterwards. Two other samples of coal and pyrites were put in a chamber at 200°. The temperature of the coal quickly increased. After 40 minutes, it reached 200°, and the coal took fire, while the pyrites had at the same time been raised only to 150°. The ignition of the coal was not at all hastened by an admixture of pyrites.

Fayol, as a result of some of his other experiments, stated that "The influence of wet weather on heaps of coal has not been sufficiently marked to be observable." On the other hand, much evidence has been given which is absolutely opposed to the above statement. In a letter to the English Commission in 1876,

¹ The Journal of the Society of Chemical Industry, Vol. 2, page 325.

² Bulletin de la Societe de l'Industrie Minerale, Second Series, Volume 8, part 3, 1879

Mr. Poole¹, Inspector of Mines, Nova Scotia, makes the following remark: "Heat has been observed in piles of slack coal that have been accumulated during the summer for the use of engines during the winter, when the season has been showery, but not when it has been dry." Much similar evidence was offered the English Commission; for, out of the 26 answers to questions as to the effect of moisture, every reply was to the effect that moisture was a source of danger. Similar evidence was given at the inquiry held by the New South Wales Commission, although, on cross examination, it was brought out that this view was more a matter of impression than of definite knowledge.

Fayol² also found that the coal of Commentry never took fire by exposure when the heaps were less than two meters deep, no matter what the lateral dimensions of the heaps might be. He also found that a mixture of dust and fragments was the most dangerous.

Some valuable evidence on the subject of the size of the storage heap was given to the New South Wales Commission by Mr. Bush³, the engineer of the Australian Gaslight Company. It appears the Australian Gaslight Company has two coal stores, one at Kent St., and the other at Mortlake. These stores are kept more or less full for gas making. The Kent St. store is filled with coal to a depth of 14 feet, the Mortlake store to a depth of 20 feet. The Mortlake store requires great care to prevent the coal from firing, whereas no case of firing from spontaneous combustion has occurred at Kent St. All other circumstances are, so far as known, exactly the same at both stores. The opinion of Mr. Bush is that the difference in the behavior of the coal in the two stores is to be attributed to the difference in depth of the coal.

"It was formerly supposed⁴ that the oxidation of pyrites (a common impurity of coal) is the initial cause of spontaneous heating. This, however, has been disproved in many tests by direct experiment, and it also appears that there is no direct relation between the pyrite content of coal and its liability to spontaneous combustion. On the other hand, if coal is wet, it has

¹ Threlfall, On the Spontaneous Heating of Coal, Jour. of the Soc. of Chem. Ind., Vol. 28, p. 763, 1909.

² For an excellent review of Fayol's monumental work on the coals of Commentry, see 1.

³ Report of the First New South Wales Commission.

⁴ From the Introduction to The Report of the First New South Wales Commission, inquiring into the causes of the firing of coal cargoes, etc.

been shown that the pyrites tends to oxidize, and in so doing may help to break up the coal and thus render it more liable to spontaneous combustion by increasing the surface. We are of the opinion, however, that the cases of spontaneous combustion of Newcastle coal are not in any way traceable to this action, since we have not been able to find that the cargoes which have fired have been unusually wet, or that the sulphur content was unusually high; in fact, the average sulphur content is only about 0.5 per cent.

"It still must be regarded as an open question, however, whether the heating of Newcastle coal is in any way dependent on the amount of moisture which it contains. On the other hand, we have the very definite experimental result of Fayol that moisture has no influence whatever on the liability to spontaneous combustion of the coal of Commentry, and yet we see that the disintegrating action of oxidizing pyrite may have an indirect effect.

"Most of the witnesses we examined were of the opinion that wet coal was more likely to fire; and some important evidence was given us by Mr. A. Ross, manager of the Wallsend Mine (Ans. 1379), and also by Mr. Reed, screen overseer, in charge of the hoppers in which the Newcastle-Wallsend Coal Company store their small coal. These witnesses stated that the temperature of the coal in the Wallsend hopper increased within a few days after a shower of rain. On visiting the hopper and digging into the coal to a depth of two or three feet, we obtained samples of coal, some hot and moist, some cool and dry. The place from which the hot sample was obtained was distant only a few feet from the place where the cool sample was taken. Chemical examination disclosed no appreciable difference between the two samples. It occurred to us that possibly the hot coal had been heated by distillation of steam from the coal below, which coal was spontaneously heated, and this we are inclined to think was really the case, for the seat of spontaneous combustion is never within three feet of the surface of a heap of coal. On drawing Mr. Reed's attention to the possibility of this explanation, he appeared inclined to agree with us (Q. 3426-8). We consider it not unlikely that the heating up of otherwise unheated coal by the distillation (and condensation) of steam may have given rise to the idea that moisture is favorable to spontaneous heating.

"Of course, if coal is red hot and small quantities of water are poured upon it, the resulting steam is decomposed by the red hot coal, and the carbon monoxide and hydrogen thus liberated burn with flaming. This fact, also, we are inclined to think may have tended to give rise to the impression that moisture assists the spontaneous combustion of coal.

* * * * *

"It is, perhaps, obvious from what has been said on the subject of the absorption of oxygen by coal, that a very important condition is the initial temperature of the coal. From two cases which came under our notice, we are inclined to think that the masters of ships are not sufficiently alive to the importance of keeping the coal away from the hot surfaces, especially when the surfaces are themselves far below the ignition point of coal. A donkey-engine and boiler, for instance, may be separated from the hold by a cement floor laid on the deck planking, and so far as we could ascertain there seemed to be an impression that the heat which could be transmitted through such a shield could have no ill effect on the coal. The fact is, however, that the rate of absorption of oxygen increases so greatly with rise of temperature that the moderate warming of the coal by a steam pipe or boiler may enormously shorten the time necessary for spontaneous combustion to set in, or may render spontaneous combustion possible in cases where it would otherwise be impossible."

These remarks apply with great force to the practice of loading coal in very hot weather. The coal lying in trucks on the dyke and exposed to the sun is loaded at a temperature which it might take months to reach if it had to generate the necessary heat by absorption of oxygen. This reasonable conclusion is supported by the fact that three very large ships were loaded together during the hot weather of January, 1896, and all of them were the victims of spontaneous combustion.

The acceleration of the rise of temperature consequent on a large initial temperature is also well illustrated by the cases of the "Knight of St. Michael", the "Morna", and the "Invernay", all of which were loaded during extremely hot weather, and all of whose cargoes became dangerously heated within a short time of loading.

The United States Admiralty¹ has made experiments and

¹ Oesterr. Zeits. Fur Berg und Hutten, Vol. 47, page 78.

The Journal of the Society of Chem. Industry, Vol. 18, page 568.

gives valuable directions for preventing the spontaneous combustion of coal. Anthracite is excluded from the inquiry since only bituminous coals are liable to catch fire. The ignition of coals may be induced by condensation and absorption of the oxygen of the air by the coal, whereby the temperature is raised so high that chemical combination between the hydrogen and oxygen can take place. This easily happens if the coal be very pure and brittle, if the outside temperature also be high, and the necessary ventilation be wanting. Another cause of ignition is the action of moisture on the sulphur of many pyritic coals, not so much from the heat of the chemical reaction as from the circumstance that the coal is split and broken up, and so fitted for the absorption of oxygen.

The arrangements for preventing ignition on board ship are not taken up, but it said that on land it is mostly the pyritic coals that take fire. Care should be taken that the coal is stored on iron floors, and covered, the height of the heap not to exceed two to two and one-half meters. For sea voyages, the coal should not be loaded earlier than one month after it has been mined.

Mr. Stelkins¹, in his report before the International Navigation Congress in 1902, stated that the tendency towards spontaneous ignition of coal increases with the height to which the coal is piled. Stacks higher than 15 ft. should not be made. Rain during and after stacking and compression caused by dumping coal from a great height on the stack, all add to the danger of ignition.

Mr. F. M. Griswold² of the Home Insurance Company, in 1904, states that spontaneous ignition is more marked in free burning or so-called "high steaming coals" including "gas coals". These coals usually contain a large amount of volatile matter and small amounts of oxygen. The tendency towards spontaneous ignition increases when sulphur or lignites are found in the coal and especially when pyrite is present. Slack, mine run, and dirty coal are dangerous because of the fine particles present, the latter gradually sifting to the bottom and being compressed.

According to Mr. Griswold, a satisfactory explanation of spontaneous ignition and combustion of bituminous coal has not as yet been made. The best authorities say it is due to chemical

¹ American Society of Naval Engineers, February, 1901

² Engineering News, November 10, 1904, page 409.

changes in the substance of the coal resulting from the absorptive powers of carbon, the latter increasing with the rise in temperature. Rise in temperature may be due to the chemical action caused by slow oxidation or to the mechanical force of pressure; both of these conditions may be stimulated by moisture and the presence of pyrites. Some claim that over $2\frac{1}{2}$ per cent of sulphur in the form of pyrite is dangerous. Various tests have been proposed to determine the liability of a coal to heat, such as the gain in weight of the coal at 250° F. and the absorption of bromine, but these tests are not valuable, as it is difficult to tell how much oxygen the coal has already absorbed. He recommends that no wood be used in the construction of bins, that all iron-work be covered with concrete, that no steam pipes or flues be near the bins, that a good circulation of air be about the sides and under the bins, and that the coal should not be piled to a depth greater than 12 ft. He also recommends that the bins be roofed, and that they contain pipes in which thermostats should be placed, and when the latter register 140° F., something should be done to stop the rise in temperature.

A. E. Dixon,¹ in 1906, stated that spontaneous ignition occurs with friable bituminous coal, and particularly with those grades containing brassy or iron pyrites; when the coal is damp, the trouble is increased. The cause is probably due to the absorption of oxygen by the carbonaceous material, just as is the case with oily cotton waste.

An article describing the coal storage department of the works of the Lackawanna Steel Company² says "Derricks are used to pile the coal and they are able to pile it to a height of 60 feet; but to avoid spontaneous combustion, it was deemed advisable to restrict the height of the piles to 20 or 30 feet."

Mr. Peter Bullock³ cites several cases of coal piles catching on fire, seemingly due to spontaneous combustion. In all, about ten or twelve cases were cited; about half of these cases he believes to be due to heating from steam pipes which were near by, for the others he gives no explanations.

Groves and Thorp⁴ state that gases occluded in the crevices

¹ Engineering News, November 10, 1904, page 409.

² Engineering Record, July 4, 1903.

³ Power, 1908, page 675.

⁴ Groves and Thorp, Chemical Technology, page 82.

or cavities of the coal escape during mining and continue to do so after storage. The inflammable nature of these gases makes them a source of great danger, for it is believed that they are the causes of many of the disastrous explosions on board vessels carrying coal as a cargo.

Parr and Barker¹, working on the gases occluded in Illinois coal, found that two active processes are set up immediately upon liberation of the coal from the vein. The first is an exudation of hydrocarbons, consisting mainly of marsh gas (CH_4), and the second is an absorption of oxygen. They found that after a period of two months practically all of the marsh gas had been liberated and, although the avidity of the fresh coal for oxygen was very pronounced, after a period of two months, active absorption of oxygen still took place.

The work of R. T. Chamberlin² on explosive mine gases and dusts confirms the above work of Parr and Barker. Working on the gases occluded in the coals of the Naomi, Monangah and Darr mines of Pennsylvania and West Virginia, the author found that after the extraneous nitrogen had been removed, methane was by far the most important gas which escaped from the bottled coal. In some tests it ran as high as 98 per cent of all the gas coming from the coal; more commonly, however, it constituted from 80 to 95 per cent of the gas liberated. The finely crushed coals gave out methane at a very rapid rate, practically all of it in a period of 8 or 10 weeks, whereas the small lump coal gave out the methane at a slow uniform rate, although after a period of 26 weeks the total volume of methane given off almost equaled that given off by the fine coal.

Working on the comparative inflammability of coal dusts from the three mines mentioned above, within a few days after the unusually violent and fatal explosions which swept all three, the author points out some valuable facts concerning the absorption of oxygen by coal. He found that comparatively little oxygen can be extracted from coal, although very large volumes of oxygen are rapidly and steadily absorbed by the coal. The experiments with coal dust indicate that, with exposure to the action of the air, there is a development of the oxides of carbon and sulphur within this dust, or of compounds which give off these

¹ University of Illinois, Engineering Experiment Station, Bulletin No. 32, 1909.

² Bulletin 383, U. S. Geol. Sur. "Explosive Mine Gases and Dusts", 1909.

gases at moderate temperatures. Coal bottled in air for a few weeks gives off a much higher proportion of carbon dioxide than if placed in a vacuum; but it does not give off as carbon dioxide, within a short time at any rate, more than a small percentage of the oxygen absorbed from the air in the bottle. Air bottled with Illinois (Cardiff mine) coal for two weeks contained at the end of that time only 1.05 per cent of oxygen and 1.59 per cent of carbon dioxide, together with 0.62 per cent methane and 96.74 per cent of nitrogen. Thus only a small proportion of the oxygen which goes into coal comes out again as carbon dioxide. The formation of water by the oxidation of a part of the hydrogen in the coal is a natural explanation for the apparent disappearance of some of this oxygen. It may also be that some of the organic compounds have been only partly saturated and hence the oxygen absorbed is not given off at once as carbon dioxide, but comes off later when the oxidation has progressed further.

Dennstedt and Bünz in 1908¹ exaggerated the conditions of spontaneous combustion by passing oxygen through a sample of coal at 135° or 150°C. The coals tested by them are divided into four classes:—

1. Coals whose temperature never rises above that of bath.
2. Coals that rise only slightly above the bath temperature.
3. Coals that rise fairly high, but will not take fire unless the oxygen supply is carefully increased with the rise in temperature.

4. Coals that take fire easily, usually in about two hours. Six typical coals were selected to determine what chemical variations accompanied the above classes. They found that coals that have been thoroughly wet kindle more rapidly than if they have been kept dry. Quoting their conclusions, we find: "Self-ignition increases in a ratio corresponding to the amount of moisture in air-dry coal; mechanically combined moisture is not meant, for the coals used gave the impression of being perfectly dry; the moisture seems to be water of constitution.

Surface absorption has the same degree of importance as the above water of constitution. The question certainly is not one of hygroscopicity, or of the hygroscopic inorganic salts present, for water-soluble mineral salts are found in very small

¹ Zeitschrift für ang. Chemie, 1908, Vol. 21, p. 1825-35.

quantities in all coals, so small that they do not even increase the surface absorption.

Moisture and its reabsorption are allied to, or controlled to a certain extent by, the organic substances and their composition. It may also be noticed here that the humic acids formed in the coals are exceedingly hygroscopic. But these cannot cause the surface absorption in the original coals, because no completely formed humic acids are present; therefore the increased surface absorption of the oxidized coals is undoubtedly due to the humic acids. The increasing Maumene number (with increasing self-ignition) is also in accordance with the idea of water of constitution, and here it is also seen that the organic substances have an influence, for the Maumene number increases in the same ratio, even in those coals that are dried in a current of carbon dioxide. It is very remarkable that these coals, dried in this way, should cause a rise in temperature when they are stirred in cold water (this property increases as self-ignition increases). The Maumene number can, therefore, well serve as a standard which would decide a coal's power of self-ignition.

Neither amount nor kind of mineral substance nor pyrite found in coal has any effect on the self-ignition; this is seen without a doubt from a consideration of the analytical data. The pyrite content is very small, and besides the pyritic coals are not the easiest to self-ignite. One could also think of certain catalytic actions; to this effect there were made numerous observations upon coals which had caused fires, and they had only a very small amount of pyrite that occurred in a fine condition. This pyrite was found in a slaty portion of the coal and upon fresh cleavage fractures in the form of a fine sulphur-colored film. But the fact that just such coals, which are very easily self-ignitable, such as Scotch coal No. 6, contained a minimum quantity of pyrite, carries one away from the above idea. The same might be thought of the hydrochloric acid soluble iron in the original coal,—that this might be due to a catalytic action, but here also the amount is small and does not grow with the degree of self-ignition so that it was not thought necessary to insert the analytical data in the tables. One could rather speak of the water-soluble iron in the oxidized coal as due to this cause; sometimes in coals that have been stored for a long time and perhaps have become wet too, an

oxidation of pyritic iron in the form of basic sulphate is found, but we did not find any increased self-ignition in them."

From the above, it seems without a doubt that the organic substances control the self ignition of coal, and it depends not so much on the amount but rather upon the kind and composition. This follows directly from the ultimate analysis; of course, the amount of organic combined sulphur and nitrogen has no effect. For it is seen that neither is found in any great amount in coals that are easily inflammable over coals not easily so. With the sulphur one could think of the formation of easily inflammable compounds, for example, carbon bisulphide. During the oxidation process, carbon bisulphide was expected, but no trace was found. Very conspicuous in the elemental composition is the proportionately small amount of hydrogen in the more inflammable coals, and the particularly larger amount of oxygen which is especially noticeable in the small amount of available hydrogen.

Quoting further from these writers:—"If the self-warming and ignition are caused by this oxidation, which we believe has been shown, then at first glance it seems a contradiction that those coals already so rich in oxygen are the most easily oxidized. But when one thinks that all coals are finally tending toward a similar or equal character or composition, then one can easily picture that a transition period of marked inflammability exists, which the easily inflammable coals have already reached. This is in accordance with the remarkable properties of the coals in Class II, which with preparatory treatment at 135°C . with oxygen, become more easily inflammable. This point seemed to be of sufficient weight to cause certain quantitative experiments to be made so as to prove it. With coal No. II (Germania) a marked change takes place by treating with oxygen at 135°C . This change consists of an addition in weight and a considerable loss of carbon dioxide and water, and this, we think, proves our assertion. Of course it is not necessary in order to change to an inflammable coal that the above must take place throughout the entire coal. It is sufficient if it happens in certain localities or perhaps only at the surface of small coal particles. That the addition in weight which takes place in oxidation, caused by the taking up of oxygen, is not substantially less in the less inflammable coals, with the exception of the altogether unflammable coal marked Nixon Navigation, rests clearly on similar reasons, (the same is

found under Table 7), from the ultimate analysis of the oxidized coal showing the addition of oxygen and the loss of carbon and hydrogen. Altogether out of place in this respect is the uninflammable coal No. 1, Nixon Navigation, which oxidizes very slowly.

"The end product of the oxidation is clearly seen to be the humic acids, and from the humic number is found without possibility of contradiction how far the easily inflammable and oxidizable coals are above the others. Less easy to account for is the fluctuating value or amount of pyridin extract, especially when one sees the content of the original and oxidized coals; but one thing is certain, that in the majority of cases the extract grows with the degree of self-ignition and is increased by oxidation. The one exception is coal No. II, which is perhaps ascribable to imperfect methods.

"Our researches show that the organic parts of the coal play two different roles which have little to do with each other. That portion soluble in organic solvents seems of similar character and composition and perhaps of similar origin as the soluble portion of Braunkohle, for example, the so-called Montanwachs, only the coal extract contains more oxygen and is therefore probably of similar origin but changed by oxidation.

"That portion of the coal insoluble in organic solvents we look upon as the real coal substance probably formed from cellulose in the original wood; and it is that substance which on further oxidation yields the humic acids and which, although not altogether still in the main part, determines the self-ignition of the coal. It contains also the unsaturated compounds upon which the iodine addition rests, which in the iodine number express themselves quantitatively, and they run parallel with the capacity for oxidation; the remarkable fluctuation of the iodine number in the original and oxidized coals we leave for the present purposely untouched.

"But, since the iodine number is so easy to determine, one has in the main a practicable means next after the Maumene number for determining the degree of danger from fire of the coal."

Summarizing their work it is seen that spontaneous combustibility increases with the following:—

1. Moisture at 105°.
2. Brittleness.
3. Iodine number.

4. Maumene number.

5. Humus number.

Graefe¹ noted that naturally weathered coal contains more ash, is of a lower calorific value, and on distillation gives less tar but has a higher paraffin content than the fresh coal.

Erdmann and Stolzenberg² found the work of Graefe to be in accord with the assumption that it is the unsaturated bodies, viz., the humus, that undergo slow oxidation. That the humus is the unsaturated body is shown by the fact that it absorbs large amounts of bromine without the evolution of hydrobromic acid, and also that it has a vigorous reaction with ozone. The humus can be extracted from the coal with alkali and separates on acidifying. A current of oxygen containing 2 per cent of ozone passed over humus in a U-tube at the rate of 500 c. c. per minute causing combustion in 23 minutes. Briquet coals coarsely powdered and moistened took fire in about 70 minutes; while dry, the temperature did not rise over 48°C. These experiments lead the authors to the conclusion that the self-ignition of small coal is due to the action of ozone.

Dry pyrite showed no increase of temperature; moist, only a 12° rise. A mixture of humus and 10 per cent of powdered marcasite (crystalline pyrite) took longer to ignite than pure humus; consequently, pyrite is not the cause of spontaneous combustion in coals.

The self-ignition of coal is probably not determined by the ozone content of the air but rather by the production of ozone, which is found by the evaporation of moisture from the surface of the moist coal. In agreement with the above statement is the fact that fires in coal heaps occur more frequently on warm, sunny days after a rain where the surface evaporation is especially great. The ozone found under these conditions immediately begins to react with, and is absorbed by, the humus substances which break up by its action in the presence of water into carbon dioxide and saturated cleavage products such as humic acid. The heat produced by this reaction accumulates when sufficiently insulated, and the rising temperature also causes the more inactive atmospheric oxygen to react, so that under favorable conditions

¹ Braunkohle, Vol. 6, 713.

² Braunkohle, Vol. 7, 69

Chemisches Centralblatt, Vol. 79, p. 456, Aug. 5, 1908.

the temperature will rise to the ignition point.

The reaction of coals with ozone as first described is a measure of their tendency to spontaneous combustion.

Moist cellulose (filter paper) showed no rise in temperature in 2 per cent ozone, wheat bran rose only 4.5° , while cotton waste soaked in linseed oil ignited very quickly.

O. Boudouard¹, 1909, in his work on the oxidation of coals and the products resulting therefrom found that in contact with the air at 100°C . coal readily undergoes oxidation; the increase in weight, through absorp^{ti}on of oxygen, in some cases being as high as 10 per cent. After oxidation in this way, coal is found to contain humic acid and to have lost its power of coking. The author then extracted the humic acid by means of potassium hydroxide solution from seven varieties of coal, both before and after artificial oxidation. The results of the fourteen analyses show that the chemical constituents of the humic substances thus obtained correspond with one or more of the following formulas:—

1. $\text{C}_{18} \text{H}_{14} \text{O}_6$ (Bertholet and Andre)
2. $\text{C}_{18} \text{H}_{18} \text{O}_9$ (Malaguti)
3. $\text{C}_{18} \text{H}_{14} \text{O}_{11}$
4. $\text{C}_{18} \text{H}_{14} \text{O}_{11}$

and that the effect of oxidizing the coal is to diminish the carbon and increase the hydrogen and oxygen content of the humic substance yielded by the coal. Concentrated nitric acid causes more complete oxidation and increases the yield of humic acid.

In an attempt to account for the coking power of coal, several samples were submitted to the effect of various organic solvents. Beyond the extraction of a small amount of resinous matter, these solvents had little if any effect. Concentrated hydrochloric, sulphuric and nitric acids, also 25 per cent potassium hydroxide solution, and finally Schweitzer's reagent, were tried. Concentrated hydrochloric acid had no effect, concentrated sulphuric and nitric acids destroyed the coking power, the 25 per cent potassium hydroxide solution and Schweitzer's reagent reduced the coking power considerably. The successive action of the potassium hydroxide solution, hydrochloric acid and Schweitzer's reagent caused the total loss of coking power; the solubility of the cellulose-like substances in the Schweitzer's reagent is the explanation

¹ Bulletin de la Societe Chimique, Vol. 5, 365; 372; 377; 380.
Compte rend. 147, 986; 148, 284; 348.

given for this result.

The humic acids found in the oxidized non-coking coals are probably the carbohydrates of the original coal in a condensed and polymerised condition. (Note: The polyatomic alcohols, sugars, etc., furnish humic derivatives by condensation and dehydration under the influence of or in the presence of heat or alkalis and acids. These humic substances thus artificially prepared are found to be very similar in composition to those extracted from peats and lignites. These facts tend to substantiate Fremy's theory¹ of the formation of peats through the fermentation of vegetable matter and the subsequent formation of coal through the agencies of heat and pressure). The fact that anthracite has not the power to make coke is easily explained; this class of coals represents the furthest progress in the metamorphosis of the plant material which no longer contains cellulose. In fact the natural or oxidized anthracites are free from humic acid. Special attention must be given to the fact that even a minute amount of humic acid is sufficient instantly to cause the loss of coking power.

Dr. Haberman² found that coal stored for a long time became unfit for the manufacture of gas, and that the coals lost in gasifying and coking value and also in heating power. He claims that the spontaneous combustion of coal is due to the absorption of oxygen by the coal substance. He gives the result of a series of experiments on spontaneous ignition in which he used 200 kilograms and then heated these samples in a fire brick retort at 50°C. The coal was supplied with air at a temperature of 24°–26°C. and practically ignited in 36–39 hours. He found that coals that oxidized the most and gave the greatest rise in temperature absorbed the largest quantities of bromine.

Parr and Francis³, working upon the modification of Illinois coals by a low temperature distillation, found that active oxidation was effected at an unexpectedly low temperature. They found that a considerable quantity of carbon dioxide was given off by the coal on distillation in an atmosphere of nitrogen and steam, and a much larger amount was given off when an atmosphere of oxygen was used. Under the latter condition an occasional rise of the temperature in the retort was noted, seemingly independent

¹ Comp. Rend. 88, p. 1048, (1879).

² Schillings' Jour. für Gasbeleuchtung u. Wasserversorgung Vol. 49, p. 419.

³ University of Illinois, Engineering Experiment Station, Bulletin 24. (1908)

of the external source of heat. This fact led to a series of experiments wherein careful temperature observations were made and in which the outgoing gas could be tested for carbon dioxide. Using an atmosphere of pure oxygen, they found carbon dioxide evolved at about $120^{\circ}\text{C}.$, the kind of coal seemingly being immaterial, for Illinois coal, Pittsburg gas coal, and anthracite were used. Ignition temperatures ranged from 160° to $300^{\circ}\text{C}.$ Using air as an atmosphere, the initial appearance of carbon dioxide was about 135° , instead of 120° with pure oxygen. This result is what would be expected, for the dilution of oxygen in the air by nitrogen would retard or lessen the activity of oxygen. At 280° a rapid rise in the oxidation temperature took place, notwithstanding the cessation of the external heat. This fact was observed on a sample of Illinois bituminous powdered coal in an atmosphere of air. Seemingly, therefore, we have here an illustration of a type of combustion which, while still below the ignition point, is still self-supporting and would be continuous, depending upon the oxygen supply.

White¹, in studying the oxygenation and weathering of coal, notes that, in general, the lower classes of coal take up oxygen on exposure to the air. This, together with some immediate loss of compressed volatile matter (cf. work of Parr and Barker) appears to mark the first phase of weathering. Later, and on prolonged exposure, there seems to be a considerable loss of carbon and hydrogen also, especially in the humic (ordinary) coals.

The weathering of the lower grades of coal, especially bituminous, lignites and peats, is marked by the accession of oxygen which is taken into combustion. This increase of the oxygen contents, which seems to indicate lack of equilibrium in the hydrocarbon compounds of the normal coal, readily permits a calorific deficiency which, on account of the high calorific value of oxygen, is often serious.

SUMMARY OF OPINIONS

Reviewing the literature given in the preceding chapter, it may be seen that opinions differ as to the real causes of spontaneous combustion. The leading factors may, however, be summed up as being the following:

¹ U. S. Geol. Sur., Bulletin 382, "The Effect of Oxygen in Coal."

1. The kind of coal, in regard to its volatile matter.
2. The purity of the coal.
3. The presence of pyrite or other sulphur compounds.
4. The temperature of the coal.
5. The size of the coal.
6. The presence of occluded gases in the coal.
7. The presence of moisture.
8. The accessibility of oxygen.
9. Pressure on the coal.

1. *Kind of Coal*.—From the ignition temperatures given by Fayol, it may be seen that only those coals (such as lignites, bituminous and semi-bituminous) containing large amounts of volatile matter, are liable to ignite spontaneously, and that anthracite with its very low percentage of volatile matter is practically entirely excluded. The results of the work of O. Boudouard, on the coking power of coals, also substantiates this view, for in his work he found that those coals richest in volatile matter (carbohydrates, cellulose, etc.) were most liable to spontaneous combustion.

2. *Purity of Coal*.—The work of our own government seems to indicate that coals of exceptional purity are more apt to heat up than coals containing large amounts of extraneous matter. This is probably due to the fact that very pure coals are able to condense and absorb the oxygen of the air much faster than other coals and so cause an increase in temperature, which finally results in the chemical combination of the oxygen and hydrogen occluded in the coal. This view is confirmed by the later work of Dennstedt and Bünz, who found that those coals causing spontaneous combustion or those coals which oxidized and increased in temperature most rapidly were remarkably free from mineral matter and pyrite.

3. *Presence of Pyrite*.—As to what part sulphur compounds, especially pyrite, play in the spontaneous ignition of coal, opinions differ greatly. Some believe pyrite to be the leading factor, while others believe it plays no part at all, or, if so, ascribe to it a position of minor importance and believe its action to be merely a subsidiary one. The oxidizing action of the air upon pyrites is, however, admitted, and the notion seems to be fairly general and

well established that pyritic oxidation tends to raise the temperature of the coal. On the other hand, it is seen from the work of Fayol, Dennstedt and Bünz, Threlfall and others that coals containing pyrite in a quantity too insignificant to be noticed are very apt to ignite spontaneously. The Newcastle coal of New South Wales is also a very good example of this class of coals.

Others, however, believe that the only influence of the pyrite is a mechanical one, in which the oxidation of the thin films of pyrite in the coal serves merely to break up the coal.

4. *Temperature of the Coal.*—Most of the authors agree that the temperature of the coal undoubtedly is one of the main factors in the whole subject of spontaneous combustion, for cases of spontaneous combustion have occurred time and again where probably they never would have occurred if there had not been an initial heating in some way or other. The New South Wales Commission thinks that the initial temperature of the coal at the time of storage or loading is one of the great factors in the subject of spontaneous combustion, the true danger of which has not heretofore been fully appreciated. Sources of heat seemingly insignificant are frequently the cause of bringing the temperature of the coal up to the danger point and so causing coals to ignite which, under carefully regulated conditions of storage, would not be at all dangerous. Numerous cases are on record where the cause of the spontaneous ignition of large coal stores and loads was finally traced back to initial heating from flues, steam pipes, or direct exposure to the sun. This increased temperature, whether coming from outside sources or from physical or chemical reactions within the coal, tends to accelerate the absorption of oxygen and thereby to raise the temperature of the coal. It also tends to drive out the inflammable gases occluded in the coal, and so greatly to accentuate the danger of spontaneous ignition.

5. *The Size of the Coal.*—That fine coal is a more active absorbent of oxygen and more liable to ignite spontaneously than large coal was shown as far back as 1868 by Richter. Practically all of the later experimenters in this field concede this to be true, for, having a greater surface, the fine particles can absorb much more oxygen than large lumps; and since this rapidity of absorption causes an increase in temperature, which in turn produces favorable conditions for further absorption and for chemical action between the oxygen of the air and the hydrogen of the coal,

the danger of spontaneous combustion is greatly increased.

Throughout the literature, warnings are found cautioning coal users and shippers against storing fine coal. Some have even advocated that only large lumps should be transported on shipboard and that these should be carefully packed by hand. The covering of coal piles with slack is to be avoided, also the coal should be handled as little as possible to avoid disintegration, for, in handling, the finer particles gradually sift down to the bottom of the pile where they accumulate and are a source of danger, inasmuch as at the center and bottom of the pile the most favorable conditions for spontaneous ignition exist. Here the coal is sufficiently insulated by the surrounding coal so as to retain all the heat that is generated. Air is accessible in sufficient amounts to cause oxidation, and still is not present in large enough amounts to conduct away the heat. The fact that friable coals are more prone to ignite spontaneously than coals not so friable, also seems to substantiate the above opinion. Dennstedt and Bünz in their work on this subject even went so far as to make a friability test on all the coals they worked with, for they conceded the danger arising from the fine coal with its great avidity for oxygen, and recommended that they considered safe to transport on board ship only those coals passing a certain standard in their friability test.

6. *Occluded Gases in the Coal.*—While it is now a well known fact that gases of an inflammable nature are occluded in coal, their relation to the spontaneous ignition of coal has not yet been clearly established. Whether the gases occluded in the coal are the real cause of spontaneous ignition is doubtful, but if the coal becomes heated up by oxidation or some other cause to a temperature high enough for the oxygen of the air to unite with these gases, then it is seen that the presence of these gases constitutes a source of danger, and then coals with large amounts of gases occluded in them would be more liable to ignite than coals containing smaller amounts of these gases.

7. *The Presence of Moisture.*—Opinions differ greatly as to what part moisture in the coal plays in the spontaneous combustion of the same. Some, as Doane, believe the moisture content of the air-dry coal to be a direct index of its power to ignite spontaneously. Evidence given to the New South Wales Commission and also the British Commission shows that coal piles are more

apt to take fire during warm weather following showers than at other times, although Fayol, as a result of experimental work, claims that the influence of the weather on coal heaps has not been sufficiently marked to be observable. Erdmann and Stolzenberg believe the spontaneous combustion of coal to be due to the formation of ozone by the action of the sun on warm, sunny days following a rain, when the surface evaporation is especially great. If this is true, moisture plays a more important part in the phenomena of spontaneous combustion than has heretofore been ascribed to it.

That the presence of moisture materially assists the pyritic oxidation is generally conceded, although whether it causes an increase in temperature or merely a disintegration of the coal due to the formation of ferrous sulphate is a matter of dispute. Others believe that the only part that moisture plays is a mechanical one, where alternate freezing and thawing break up the coal into smaller particles and so expose more surface to the oxygen of the air. Again, it is thought that aside from increasing the pyritic oxidation, moisture acts as a catalytic agent between the carbon and hydrogen or unsaturated bodies of the coal and the oxygen of the air. Perhaps, as Erdmann and Stolzenberg have suggested, this reaction may consist of the formation of ozone which is immediately absorbed by the coal. This idea of catalytic action on the part of the moisture is substantiated to some extent by the fact that some coals containing minimum amounts of pyrite are nevertheless very liable to spontaneous ignition; and coals of this class, viz., the Newcastle and Scotch coals, have been known to cause fires.

8. *The Accessibility of Oxygen.*—That the combination of oxygen with the constituents of the coal causes a rise in temperature seems to be firmly established. Which particular constituent is the cause of the rise in temperature has not, however, been shown with any great degree of certainty. The presence of humic acid in the oxidized coal leads one to believe that the oxygen combines with some of the unsaturated humus bodies, such as the polysaccharides. That this humus substance is an unsaturated body is shown by the fact that it absorbs large amounts of bromine without the evolution of hydrobromic acid. In fact, Fischer goes so far as to devise a practical test to determine the safety of a coal by means of this reaction with bromine.

The idea is also held that the oxygen of the air combines directly with the carbon and hydrogen of the coal and so causes an increase in temperature. If amorphous carbon (charcoal and lampblack) can be oxidized to carbon dioxide on exposure to the air by means of bacteria, as has been proved by Potter,¹ the oxidation of the carbon of the coal is very probable.

The presence of oxygen is therefore to be avoided and the old idea of thoroughly ventilating the coal piles by free access of air is gradually being dropped, and at the present, authorities deem it advisable to keep the coal away from the air as much as possible, either by submerging it under water or storing the coal in covered concrete bins. If ventilation is used to lower the temperature of the coal, it should be through pipes, so that the cooling air cannot come in contact with the coal at all.

9. *Pressure on the Coal.*—The belief that pressure on the coal is one of the leading factors in the spontaneous ignition of coal seems to be gaining ground, and because of this fact it is advocated that coal heaps should not be any higher than 15 to 20 ft. The experience of Mr. Bush in this respect (see page 69) is certainly very startling, and in a store of that size the question is very probably one of pressure rather than radiation, although, in smaller storage units, it would probably be hard to decide whether the cause of the spontaneous combustion was due to pressure or lack of proper insulation of the heat generated within the pile.

It will be highly suggestive to compare this summary of opinions with the summary at the close of the experimental part of this work. The evidence of the oxidation of the various coal substances is there enumerated, and is in close agreement with the various investigators cited above, but the conclusions as to the part played by each is different; namely, that the oxidation (a) of the unsaturated humus bodies; and (b) of pyrites are direct contributors to the heat conditions which set in motion the more advanced and vigorous phases of oxidation. The activity of these initial stages is there designated as directly dependent upon fineness of division, moisture and accession of heat from physical or external sources. With these propositions established, the real importance of these initial activities is at once apparent and the fundamental principles which must be observed in remedial processes are made evident.

¹ Proc. Roy. Soc. London (B), Vol. 80, p. 196.

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